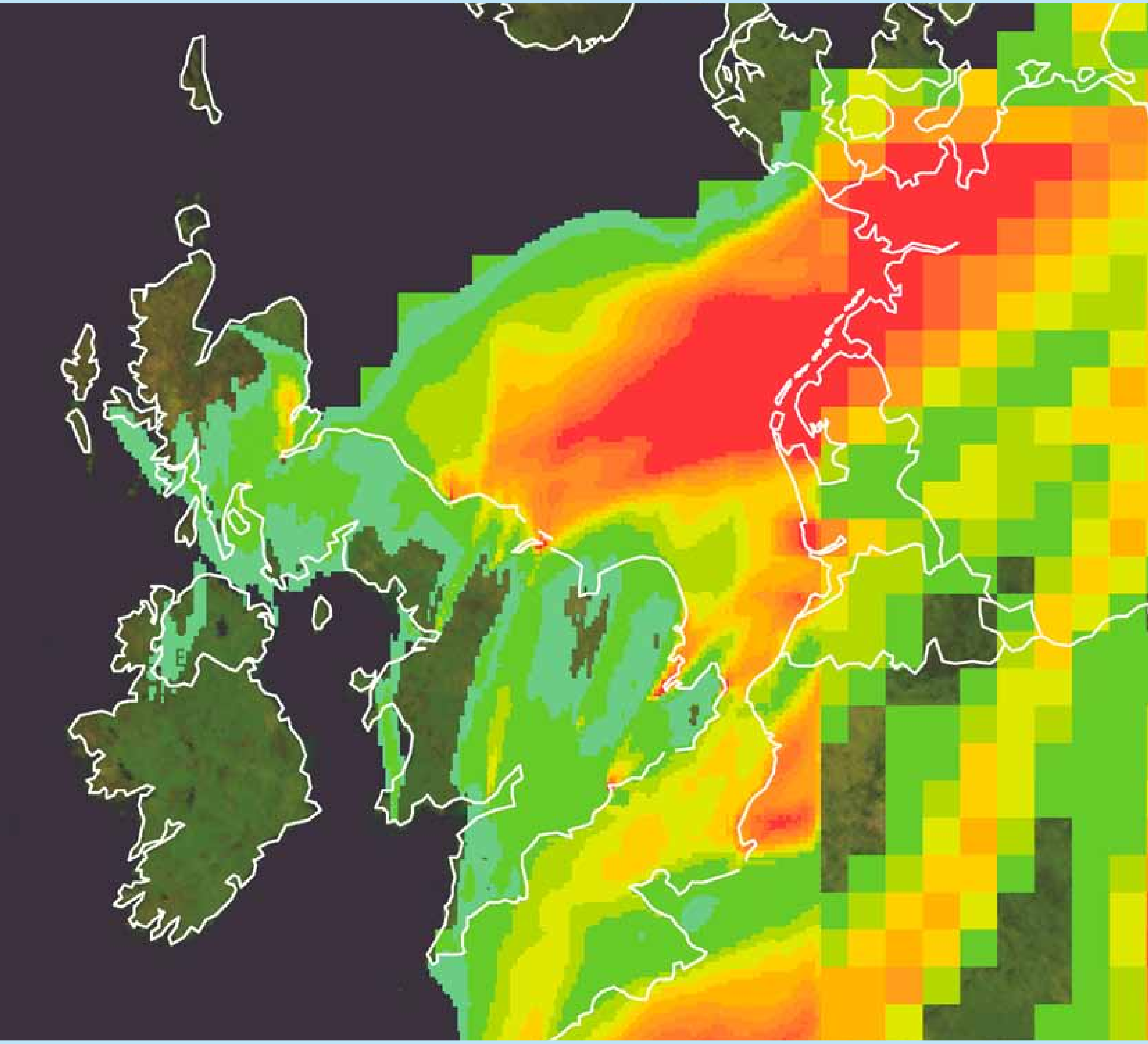
REVIEW OF TRANSBOUNDARY AIR POLLUTION (RoTAP):

Acidification, Eutrophication, Ground Level Ozone and Heavy Metals in the UK



Prepared for: Department for Environment, Food and Rural Affairs;
Scottish Government; Welsh Assembly Government; and
Department of the Environment in Northern Ireland

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This report was prepared for the Department for Environment, Food and Rural Affairs; Scottish Government; Welsh Assembly Government; and Department of the Environment in Northern Ireland as part of the Defra-funded contract, Review of Transboundary Air Pollution (RoTAP) (Defra Contract Number AQ0703).

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Cover Image represents the daily average particulate sulphate surface concentration over the UK for 16th May 2006, calculated using the EMEP4UK atmospheric chemistry transport model (v3.7). The model uses a fine grid resolution of 5 km^2 over the UK nested within a coarse European domain (http://www.ceh.ac.uk/sci_programmes/EMEP4UK.html). The concentrations range from ~0.3 $\mu gS/m^3$ (light green) to ~1.5 $\mu gS/m^3$ (red), with a prevailing westerly wind. Plumes from some of the main UK sources of sulphur are clearly visible.

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Executive Summary

This report provides a detailed overview of the current status of transboundary air pollution in the UK. It reviews the current state of air pollution issues, evaluates the extensive measurements of atmospheric pollutants and their effects, and provides a synthesis of current understanding. The review focuses on the main causes of acid deposition, eutrophication, ground level ozone and heavy metal pollution in the UK, namely sulphur dioxide (SO_2), nitrogen oxides (NO_x), ammonia (NH_3), aerosols (particulate matter), heavy metals, nitric acid (HNO_3) and ozone (O_3). A summary of the current European status is included to provide a wider perspective for the assessment.

Emissions of primary pollutants contributing to transboundary air pollution have changed substantially during the last 30 years, mainly in response to international control measures such as the UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP), and the EU National Emission Ceilings Directive (NECD) which set ceilings for the emissions of key atmospheric pollutants including sulphur dioxide (SO_2), oxides of nitrogen (NO_x) and ammonia (NH_3) for European Community Member States, which the UK had to achieve by 2010.

The report reviews trends in the emission, concentration and deposition, and effects of atmospheric pollutants on soils, vegetation and freshwaters. These may be summarised as follows:

Emissions

- Emissions of sulphur dioxide have decreased by 94% between 1970 and 2010. The UK met the NECD target for 2010, with emissions 31% below the target value.
- Emissions of nitrogen oxides in recent years have not been reduced by as much as policy-makers intended, decreasing by 58% between 1970 and 2010. The UK met the NECD target for 2010, with emissions 5% below the target value.
- Emissions of ammonia have decreased by 21% between 1990 and 2010. The UK met the NECD target for 2010, with emissions 4% below the target value.
- Emissions of non-methane volatile organic compounds (NMVOCs) have decreased by 61% between 1970 and 2010. The UK met the NECD target for 2010, with emissions 34% below the target value.

Concentrations and deposition

- Concentrations of sulphur dioxide in UK surface air have declined to values which no longer pose a direct threat to sensitive plant species. Sulphur deposited in the UK has decreased by 80% between 1986 and 2006, allowing partial recovery of sensitive ecosystems from the effects of acidification.
- Concentrations of oxidised nitrogen in surface air (as nitrogen dioxide) have declined, approximately in line with emission reductions. However, deposition of oxidised nitrogen has not changed in response to the reduced emissions

due to a change in the chemical reactions occurring in the atmosphere. Nitrogen dioxide (NO_2) in the atmosphere is now more rapidly converted to nitric acid and particulate nitrate than it was in the late 1980s. The atmospheric lifetime of NO_2 is shortened with a subsequent reduction in the distance it travels in the atmosphere before removal by deposition. An important consequence of these changes is that the fraction of UK emissions of NO_2 exported to other countries has declined over the last 30 years, and especially over the last 10 years. Exports declined by 50% while deposition in the UK declined by only 22% between 1986 and 2007, a period in which emissions declined by 50%.

- Concentrations of reduced nitrogen (as ammonia) have changed little since 1990, with small increases in background areas and small reductions in regions dominated by pig and poultry sources.
- The total deposition of nitrogen (including both oxidised and reduced forms) in the UK has not changed significantly between 2000 and 2006, at 400 kt-nitrogen per year, and has changed little over the period 1987 to 2006.
- Peak ground level ozone (O_3) concentrations declined by about 30% between 1986 and 2007, while annual mean ozone concentrations in the UK increased by 0.2 ppb per year, representing an increase of approximately 15% over the 20 years.
- The changes in ozone climatology have moved the main focus of concern over ground level ozone from peak exposures to the growing mean and background contributions.

Effects

- Soil acidity has declined widely in the UK in response to reduced acid deposition. There has been a reduction in the area of Broad Habitats exceeding critical loads for acidity from 71% in 1996-98 to 54% in 2006-08. Exceedance is projected to decline to 40% by 2020.
- Topsoil nitrogen (N) concentration has decreased in many habitats despite continued N deposition. A concomitant increase in carbon:nitrogen (C:N) ratios implies that either N loss has increased or that the N signal has been diluted by increased C fixation by plants. There are indications that N deposition has affected soil microbial activity, increasing N availability to plants.
- There is widespread evidence of the ongoing recovery of UK freshwaters from the effects of acidification, with reductions in acidity and labile aluminium, increases in alkalinity and an increased occurrence of acid-sensitive biota. Recovery is a slow process and is slower in afforested catchments. In some cases ‘recovering’ biological communities have been shown to differ from those that characterised sites when they were less acidified in the past and it is unlikely many will ever fully resemble their pre-acidification state as a result of other physico-chemical changes to habitats, and physical and ecological restrictions on the re-establishment of species. Levels of acidity in significant numbers of lakes and streams in the most acidified regions currently remain above the hypothetical critical limit, used for setting critical loads. Large increases in dissolved organic carbon in UK freshwaters over the last 20 years

have been observed and these are most probably a consequence of reduced acid deposition.

- There is strong evidence that deposited nitrogen has reduced the diversity of plant species per unit area in a range of sensitive habitats of high conservation value over large areas of the UK. Nitrogen deposition on sensitive terrestrial habitats throughout the UK exceeds the critical load in 58% of their area, a value which has hardly changed since the mid-1980s. This figure is only expected to decrease to 48% by 2020. There is a strong body of coherent evidence that exceedance of these critical loads is associated with adverse effects on terrestrial biodiversity at a UK scale. There is evidence that the effects of dry-deposited reduced nitrogen (as NH_3 gas) are greater per unit deposited nitrogen than those of the equivalent wet-deposited nitrogen (as ammonium (NH_4^+) or nitrate (NO_3^-)).
- Critical levels of ozone for agricultural crops, forests and semi-natural vegetation are exceeded over much of the UK. Exposure to typical summer concentrations of ozone has been calculated to reduce the UK yield of wheat and potato production by 7% and 2% respectively.
- Current nitrogen deposition in the UK is enhancing carbon sequestration by forests, but ozone is reducing this effect. In addition, soil fluxes of nitrous oxide (N_2O) and methane (CH_4) are enhanced by nitrogen deposition. However, the combined effects of air pollutants on the UK greenhouse gas budget have not been quantified.

European/global perspectives

- European emissions of sulphur, nitrogen and the precursors of ground level ozone continue to decline in response to policy actions and in the case of acidification it is a success story with regard to emissions, concentrations and deposition. Much more action on nitrogen will be required to achieve a similar opportunity for chemical and ecological recovery from the effects of eutrophication.
- For ground level ozone, the benefits of reductions in peak values as a consequence of reductions in European emissions of oxidised nitrogen and volatile organic compounds, have been eroded substantially by emissions elsewhere throughout the northern hemisphere, including from international shipping, which are driving up the background ozone concentrations. To solve ground level ozone problems in the UK and elsewhere, it will be necessary to develop policies and emission control measures at the hemispheric scale.

Technical Summary

Transboundary air pollution issues have been important subjects for science and policy in the UK since the United Nations Conference on the Human Environment 40 years ago. The development of strategies to reduce the effects of transboundary pollution on human health and ecosystems has evolved along with scientific understanding of the subject through this period. This report aims to review the current state of rural air pollution issues in the UK, evaluate the extensive measurements of atmospheric pollutants and their effects, and produce a synthesis of current understanding which will be used to determine air quality policies. The review focuses on the main chemicals causing acid deposition, eutrophication, ground level ozone and heavy metal pollution in the UK, namely sulphur dioxide (SO_2), nitrogen oxides (NO_x), ammonia (NH_3), aerosols, heavy metals, nitric acid (HNO_3) and ozone (O_3). This report reviews all of the current data available on these pollutants and their contribution to acidification, eutrophication, ground level ozone and heavy metal deposition in the UK. The report covers:

- Trends in emission, concentration and deposition of the main atmospheric pollutants.
- Changes in the atmospheric processing of pollutants and their significance for policy.
- Changes in the exceedance of critical loads and levels for all pollutants and UK ecosystems for which this methodology applies.
- Evidence of chemical and biological recovery from the effects of acid deposition.
- Evidence of any changes in the eutrophication of UK ecosystems.
- Evidence of any changes in the effects of ground level ozone on UK ecosystems.
- The use of long-range transport models to assess the prospects for further change during the coming decade.
- An assessment, where possible of the effects of climate change on acidification, eutrophication, heavy metals and ground level ozone.

The scope of the report is therefore broad, and this summary section identifies the main findings. The subject is presented in order, following the pollutant pathway from source to receptor, as outlined in the chapters summarised below.

Emissions (Chapter 2)

Significant reductions in emissions from most pollutants have been achieved. Whilst there have been substantial reductions from industry, much of the observed decrease in emissions has been caused by fuel switching to natural gas use, and the increased use of abatement technologies.

Emissions of sulphur (S) have decreased by 94% from 1970 to 2010, and are projected to continue decreasing. The UK met the EU National Emission Ceilings Directive (NECD) 2010 target for sulphur dioxide, with emissions 31% below the target value.

Emissions of nitrogen oxides (NO_x) in recent years have not been reduced by as much as policy-makers had intended decreasing by 58% between 1970 and 2010. This is because the real world performance of new cars has given rise to higher emissions than originally estimated from dynamometer studies. Validation studies show divergence of trends between roadside concentrations and road transport emissions of NO_x. In addition, there was an increase in the proportion of coal used in electricity generation between 2000 and 2006. The UK met the NECD target for 2010, with emissions 5% below the target value.

Emissions of ammonia (NH_3) have decreased by 21% between 1990 and 2010. The national totals are sensitive to the emission rates assigned to cattle, and there is significant uncertainty associated with NH_3 emission data. The UK met the NECD target for 2010, with emissions 4% below the target value.

Emissions of non-methane volatile organic compounds (NMVOCs) have decreased by 61% since 1970. The UK met the NECD target for 2010, with emissions 34% below the target value.

Emissions of heavy metals have decreased significantly since 1970. For most metals, this has been caused by the reduced consumption of coal and the decline of heavy industry in the UK. For many metals, processes in the ferrous and non-ferrous metals industry are now the source of some of the most significant emissions. There is poor agreement between model results and measurements, which suggests that the emissions from some sources are underestimated by, or missing from, emission inventories.

Rather than climate change itself, it is the policies put in place to tackle climate change which have the potential to affect the emissions of air quality pollutants. Most climate change policies should reduce emissions of air quality pollutants, but some may give rise to increased emissions. The latter policies include the increased use of biomass, or carbon capture and storage in electricity generation.

Concentrations and deposition of sulphur, nitrogen, base cations and ozone in the UK (Chapter 3)

Ambient rural concentrations of sulphur dioxide (SO_2) and nitrogen dioxide (NO_2) have declined following reductions in emissions, by 90% and ~50% respectively, between 1987 and 2008. Concentrations of NH_3 remain high over extensive areas of the UK and have changed little over the last decade.

Concentrations of acidity, sulphate and non-marine chloride in rain have declined on average over the last 20 years, by 85%, 75% and 95% respectively, but quantitatively the trend is dominated by sulphate which accounts for 75% of the trend in deposited acidity.

Deposition velocities of SO_2 have increased as the UK countryside has steadily become a more effective absorber of SO_2, further decreasing ambient concentrations. Overall, dry deposition has declined by 93% whereas wet deposition has declined by 57% leading to the greatest benefits of emission reductions observed in the source regions of central and eastern England.

The total deposition of nitrogen (which is fairly evenly split between the oxidised and reduced forms) has changed little (-13%) between 1988 and 2008 from 389 kt yr^1 to 336 kt yr^1, despite large (50%) reductions in emissions of NO_x and 18% reductions in emissions of NH_3.

Substantial non-linearities in the relationship between emission and deposition in the UK for sulphur and nitrogen compounds have been observed. These are quite well understood for sulphur compounds, but in the case of oxidised nitrogen, while they imply a steady increase in rates of oxidation of NO_2 with time, the mechanistic detail remains largely unknown.

The main consequence of the ~58% reduction in UK emissions of oxidised nitrogen between 1988 and 2010 is that exports from the UK have declined by nearly 50%; however, deposition within the UK has declined by only 23%.

Peak O_3 concentrations in rural areas of the UK have declined by about 30% between 1986 and 2008, while background concentrations have increased by roughly 0.2 ppb annually. Hot, dry summers such as that in 2003 still lead to high concentrations. The climatology of ozone in the UK has changed between 1986 and 2008, with increased winter and spring values and smaller peaks in the summer. This changes the focus of concern over ozone and the methods of control towards hemispheric rather than country or regional solutions. The effect of climate change on atmospheric processing and deposition of pollutants has not received much attention; however, in the case of ozone, the effects over polluted regions between 2000 and 2050 are expected to reduce the benefits of controls on ozone precursor emissions.

Modelling the concentrations and deposition of pollutants over the UK (Chapter 4)

Atmospheric Transport Models (ATMs) are powerful tools for providing detailed estimates of the spatial distribution of concentration and deposition of pollutants. They can be applied to estimating past and future trends as well as attributing emissions sources to the pollutants. Accurate modelling of pollutant deposition and concentration requires appropriate parameterisation of meteorological, physical and chemical processes in the atmosphere and detailed mapping of pollutant emissions. Simple models have been applied to estimate trends and uncertainty in sulphur and nitrogen deposition in the UK. The preliminary results from complex models are available. Their further application is currently under development.

The deposition of sulphur, oxidised nitrogen and reduced nitrogen in the UK are predicted to decrease between 2005 and 2020 by 47%, 32% and 16% respectively. Reduced nitrogen deposition is expected to become relatively more significant compared to oxidised nitrogen and sulphur deposition. Policy to further reduce nitrogen deposition and acid deposition will need to focus on control of emissions of ammonia.

International shipping emissions contributed 18% and 19% respectively of the deposition of oxidised nitrogen and sulphur in the UK during 2005. With the implementation of the MARPOL Convention on emissions from international shipping, sulphur deposition from shipping will be greatly reduced by 2020. The contribution of emissions of nitrogen oxides (NO_x) from international shipping to oxidised nitrogen deposition is likely to remain high at approximately 30%.

Models are able to simulate high ozone concentrations, such as those measured during the 2003 heatwave. However this requires accurate simulation of both local and mesoscale meteorology. There has been a significant decline from 1990 to 2005 in episodic peak ozone concentrations at central England locations that is accounted for by European NO_x and volatile organic compound (VOC) emission reductions. Year-to-year variability in intercontinental transport has completely overwhelmed the slight downwards trends that would be expected in annual mean ozone concentrations at these same locations from NO_x and VOC emission reductions.

Modelled AOT40 (a metric of vegetation exposure to ozone) shows a decreasing gradient across the country from south to north due to imports from mainland Europe. Future work will focus on the derivation of ozone flux metrics as a routine output of ozone policy models as they are considered to be a more appropriate measure of the effects of ozone on crops and vegetation.

Effects on soils, freshwaters and vegetation (Chapter 5)

Soils

Five major soil monitoring programmes show increases in soil pH, primarily in response to the decline in sulphur (S) deposition. A range of factors are identified as affecting the rate of change of soil acidity including soil type, historical S deposition, inherent soil pH, rate of soil carbon (C) accumulation, and past and continuing lime additions. Some studies indicate that recovery may be slower than expected in organic soils as a result of buffering by organic acids.

There has been a reduction in the area of broad classes of terrestrial habitat exceeding critical loads for acidity from 71% of ecosystem area using 1996-98 acid deposition data, to 54% using deposition data for 2006-08; exceedance is predicted to decline to 40% in 2020.

Topsoil nitrogen (N) concentration has decreased in many habitats despite continued N deposition. A concomitant increase in carbon:nitrogen (C:N) ratios implies that either N loss has increased or that the N signal has been diluted by increased C fixation by plants. There are indications that N deposition has affected soil microbial activity, increasing N availability to plants.

There is increasing interest in the effects of atmospheric deposition, and in particular nitrogen deposition, on greenhouse gas emissions and carbon storage in soil and thus climate change. There are three large-scale soil monitoring programmes which have studied changes in soil carbon concentrations over time. Two suggest no change whilst one reported major loss. Experimental data support the potential for nitrogen deposition to change carbon fluxes and storage, and greenhouse gas emissions.

The interaction of climate change with air pollution impacts is potentially wide-ranging. One analysis of climate change effects on the area of conifer forests currently receiving nitrogen and acidity in excess of their critical load indicates only a 1-1.5% change in area of exceedance due to changes in rates of biogeochemical cycling. However, other habitats may be more sensitive. The interaction of air pollution and climate change may also bring about a change in sensitivity to extreme events, such as prolonged drought and damage by pathogens and pests, caused by air pollution.

The changes observed in soil due to air pollution are interlinked with those observed in air, water and vegetation and together affect a wide range of ecosystem services. These include climate regulation, nutrient cycling, support of biodiversity, and regulation of water flow and quality.

Freshwaters

Over the past two decades concentrations of sulphate from non-marine sources (xSO_4^{2-}) in UK acid-sensitive surface waters have fallen substantially and in line with reductions in xSO_4^{2-} deposition in most regions, although concentrations in the most acidified regions remain several times higher than those in the lowest deposition region in north-west Scotland.

Nitrate (NO_3^-) concentrations show little evidence of decline and in some waters have increased over the last 20 years. Interannual variability is linked to variability in climate. Stable isotope analysis reveals that most N deposition is microbially processed prior to NO_3^- being leached and emphasises that deposited N, regardless of the oxidised or reduced form, may make a net contribution to the acidity of receiving waters.

Considerable uncertainty remains with respect to the future behaviour of N in catchments, and the extent to which further accumulation of N within soils and interactions with future climate change may affect the delivery of acidifying NO_3^- to surface waters.

In waters without forested catchments, acid neutralising capacity (ANC) has increased in proportion to reductions in xSO_4^{2-}. There has been a substantial reduction in the habitat area which exceeds the critical limit for ANC according to the First-order Acidity Balance model (FAB). Reductions in hydrogen ion (H^+) (i.e. increased pH) and labile aluminium (Al) concentrations reflect the increased ANC. Sharp falls in labile Al have occurred in the most heavily acidified streams, particularly with respect to episodic maxima associated with hydrological extremes and sea-salt events, and this should have reduced considerably the stress on acid-sensitive aquatic organisms. Labile Al, possibly the most biologically damaging product of acidification, remains substantially above pre-acidification values in the more acidic waters in several regions, and may still represent a barrier to biological recovery.

In more acidified lakes and streams pH is beginning to respond more rapidly to increases in ANC as the buffering effect of aluminium declines. Small further reductions in the acid load at these sites should result in significant further increases in pH.

Dissolved organic carbon (DOC) concentrations have increased in an apparent response by soil organic matter to falling levels of soil acidity, and/or ionic strength, and have partially offset increases in pH predicted by process-based models.

Surface waters with catchments covered by commercially-operated coniferous forests tend to be more acidified than moorland equivalents and their chemistry has not recovered as rapidly in some cases. However, chemical responses are strongly dependent on the stage of the forestry management cycle.

Evidence for biological response to improving water chemistry is widespread but communities often still differ markedly from those in non-acidified control sites. Biological recovery is expected to lag behind chemical recovery for various physical and biological reasons. Given the relatively recent improvements in water chemistry it is far too early to draw firm conclusions on the long-term consequence of emissions reductions on acidified aquatic ecosystems. Reasons for the muted nature of biological response are not always clear, although in streams acid episodes clearly restrict the rate of biological recovery.

Comparisons between diatoms in lake sediments and those in sediment traps provide robust indications of the current state of ecological recovery relative to the pre-industrial state. These suggest that in some cases aquatic ecosystems may be developing along new trajectories, possibly due to effects of other drivers such as changing climate or N deposition.

Experimental studies of upland UK lakes show that primary productivity of phytoplankton is limited as frequently by nitrogen as by phosphorus, and suggest that atmospheric N deposition is changing the ecology of these systems by acting as a nutrient.

Vegetation

Critical loads for effects of nitrogen deposition on sensitive habitats are exceeded for 58% of their area in the UK, and exceedance is only expected to decrease to 48% by 2020. Taken together, the data from field surveys and experimental studies provide a strong body of coherent evidence that exceedance of critical loads of nitrogen deposition is associated with adverse effects on terrestrial biodiversity at a UK scale.

There is strong evidence that nitrogen deposition has significantly reduced the diversity of plant species per unit area in a range of habitats of high conservation value over large areas of the UK. The loss of plant diversity is primarily due to a decline in frequency of species adapted to low nutrient habitats. Where overall species diversity has not changed, species adapted to low nutrient habitats have been replaced by species adapted to higher nutrient availability, with undesirable implications for habitat conservation. There is little evidence of further declines in diversity over the last 20 years in areas of high N deposition and much of the decline in species diversity may have preceded the 1980s. However, there is evidence that current nitrogen deposition in many parts of the UK is associated with further declines in the frequency of sensitive plant species.

There is evidence that effects of dry-deposited gaseous ammonia are greater than those of the equivalent dry deposition of gaseous nitrogen oxides and wet deposition of nitrogen. The critical level of ammonia for lower plants is exceeded over 69% of the UK, and that for higher plants is exceeded over 19% of the UK; hence ammonia sources should be a priority focus for emission control.

Northern hemisphere background concentrations of ozone have now increased to a level which may have adverse effects on vegetation in the UK, especially during spring. The changes in ozone exposure that have occurred over the last 20 years are not captured by the AOT40 index. This index is flawed for risk assessment in the UK, and should be replaced by methods based on modelled flux (POD_Y) into the leaf. However, these methods need validation and incorporation into appropriate models before they can be used for routine risk assessment at the UK or European scale. Flux-based models estimate that ozone reduces the yield of wheat in southern Britain by between 5% and 15% in a typical summer. The loss in total national yield in 2000 was approximately 1.2 million tonnes, equivalent to 7% of production. The loss of potato yield was equivalent to 2% of production. Flux-based critical levels for effects on major forest trees are exceeded throughout the UK. Flux-based critical levels are not available for semi-natural vegetation, but those based upon the AOT40 index are exceeded over large areas of sensitive habitats.

Current rates of nitrogen deposition are enhancing, but current ozone concentrations are reducing forest growth and carbon sequestration across Europe. In grassland ecosystems, both nitrogen deposition and ozone have similar effects on major ecological functional groups. However, the combined effects of nitrogen deposition and ozone in the UK have not been quantified.

Nitrogen deposition reduces the conservation value of sensitive priority habitats, and is a significant barrier to the UK achieving its targets within the Habitats Directive and Biodiversity Action Plans. Ozone may have similar effects, but there is a much smaller body of supporting evidence.

Heavy metals (Chapter 6)

The UK National Atmospheric Emissions Inventory (NAEI) provides spatially disaggregated emissions of arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), selenium (Se), tin (Sn), vanadium (V) and zinc (Zn) for known sources. UK emissions of Pb, Cd and Hg have significantly decreased since 1990 in compliance with the 1998 UNECE Protocol on Heavy Metals. Additional legislation exists at national and local scales to control emissions from industrial activities including municipal solid waste (MSW) incinerators.

Concentrations of heavy metals in air have declined since the 1970s. Concentrations in the atmosphere are generally highest in the south and east of the UK, although deposition, which is strongly influenced by rainfall, is highest in mountainous areas in the north and west of the UK.

Measured air concentrations and total deposition imply much larger emissions of most metals than are recorded by modelling studies using the official emission inventory, by factors ranging from 2 to 10. The emissions of Pb, Zn and Cu are among those for which the inventory is least satisfactory. For a few metals, including Hg and V, the deposition values are below reported UK emissions. Although some of the factors responsible for this discrepancy, such as wind-driven resuspension of surface particles, have been identified, there is currently too little quantitative information to rationalise emissions and deposition.

Soil concentrations of Ni, Zn and Cd are likely to deline over this century, but Cu and Pb concentrations are unlikely to decline for centuries. Concentrations of Pb, Hg and probably Cu in some habitats, such as freshwater lochs, may still be increasing. In many soils there is a large legacy of historic deposition which is currently not available to biota because it is strongly bound to soil organic matter. Any decrease in soil organic matter, for example in response to climate change, would risk releasing this store of metal into the environment in a potentially bioavailable form.

Critical loads based upon ecosystem effects have been calculated for Cd, Pb, Cu, Ni and Zn for six UK habitats. Exceedances of critical loads for non-forest and managed coniferous woodland are low for all metals, although over 50% of areas of managed broadleaved woodland and unmanaged woodland exceed the critical loads for Cu, Pb and Zn.

Critical limits for the effects of heavy metals on biota reflect current concentrations in soil, which may arise from current or past deposition, underlying geology or other inputs to managed systems. Where these limits are exceeded there is a risk to biota; for Cu over 50% of broadleaved woodland is at risk, and for Zn over 25% of all six UK habitats are at risk.

The European and global perspectives (Chapter 7)

European emissions of sulphur dioxide have continued to decrease since 1980 and as a consequence of agreed policy actions, will continue to decrease over the next 10-15 years. By 2020 emissions are expected to be less then 10% of those in 1980. Emissions of nitrogen oxides are also decreasing and by 2020 will be reduced by about 70% compared to the situation in 1990. For ammonia, the emission reductions have been less and the emissions in 2020 will be reduced by approximately 40%.

Emission reductions have improved the European situation with respect to exceedances of critical loads and levels. The ongoing reductions will further improve the situation, particularly with respect to acidification. For both acidification and eutrophication, there will still be large exceedances by 2020 indicating the need for further significant reductions of atmospheric emissions of ammonia and nitrogen oxides (NO_x).

The relative importance of emissions from shipping has increased between 1986 and 2008 and significant emission reductions are needed to meet critical loads and levels. Recently agreed emission controls on sulphur dioxide will significantly improve the situation but the impact from NO_x emissions will probably remain at a similar level as today for the foreseeable future.

UNECE and EU strategies to control emissions of NO_x and volatile organic compounds (VOCs) have resulted in reductions in peak ozone concentrations. However, ozone concentrations large enough to damage vegetation are still common. Over 600 validated records of visible injury to crops and species of semi-natural vegetation have been identified throughout Europe over the last 15 years. The geographical distribution of recorded field effects of ozone is more consistent with exceedance of critical levels based on flux into the leaf than critical levels based on AOT40. In part the problems require further reductions of the ozone precursor gases within Europe, but to be fully effective in protecting ecosystems in Europe emission reductions on a much larger geographical scale (i.e. hemispheric) are required.

Current capability to quantify air pollution–climate change feedbacks is quite immature, as the changing climate introduces feedbacks that are poorly understood.

Changes in transboundary transport of pollution as a consequence of climate change are small relative to the impact of climate change on the emissions, atmospheric processing and deposition of air pollutants.

Intercontinental transport of ozone has become more significant as global emissions of ozone precursors have grown in recent years. North Atlantic shipping emissions of sulphur and NO_x are of particular importance for European air quality as emissions within Europe have decreased.

Recovery (Chapter 8)

Recovery of air quality throughout the UK continues, dominated by reductions in sulphur concentrations and deposition. The deposition of nitrogen in the UK, in oxidized and reduced nitrogen forms has changed little over the last 20 years, despite substantial reductions in emissions, thus the conditions under which recovery might begin have yet to be established.

Peak ground level ozone concentrations have declined by approximately 30 ppb (~25%) as a consequence of controls on precursor emissions in the UK and more widely throughout Europe. However, hemispheric background levels have steadily increased over the last 20 years due to increases in emissions of ozone precursors throughout the northern hemisphere. With these changes in the ozone climatology, ground level ozone remains a significant threat to vegetation in the UK.

Chemical and biological recovery of acidified soils and freshwaters is clearly progressing throughout the UK with reductions in acidity and the reappearance of acid-sensitive biota in freshwaters and reduced acidity in soils. However, the end-point of the recovery trajectory remains unclear and could differ significantly from pre-acidification as a result of position in the landscape and changes in climate, land use and future levels of nitrogen deposition.

There remain large areas in exceedance of critical loads of acid deposition, and these are expected to decline over the coming decade, from 54% in 2006-08 to 40% of UK habitats in 2020. Soils, freshwaters and vegetation show no significant signs of recovery from the widespread effects of eutrophication consistent with no significant changes in areas of critical loads exceedance. Current (2006-08) exceedances of critical loads for eutrophication of 58% of UK habitats by area are expected to decline to 48% by 2020. Rates of biogeochemical recovery in terrestrial systems are expected to be much faster than ecological recovery rates in higher plant species. Experience from other countries such as the Netherlands shows that active management is required to rapidly restore sensitive habitats.

Reductions in SO_2 concentrations have led to a recolonisation of sensitive lichen and bryophyte species in large areas of the country. Foliar sulphur concentrations of major tree species, grassland and crops have declined in response to reduced sulphur deposition, and in some cases have now reached deficiency levels.

Climate change may influence the processes driving acidification, eutrophication and ground level ozone but there are both negative and positive interactions. Under conditions of constant acid deposition, any future increase in rainfall or sea-salt deposition in response to an increase in storminess is likely to increase the severity of acid episodes in acidified streams and have a deleterious effect on further ecological recovery.

The quantity of metals, such as copper and lead, strongly retained in soil following atmospheric deposition will decline very slowly, taking hundreds of years to respond to recent reductions in deposition. However, the amounts of less strongly bound metals in soil, including nickel, zinc and cadmium, will decline in response to reductions in deposition during the present century. A consequence of these long time constants for the soil processing of metals is that the main problems of soil contamination by metals in the UK are the legacy of historical deposition. However current deposition of copper, lead and zinc still presents a threat to the soils of some woodland habitats.

Chapter 1 Introduction

Transboundary air pollution issues have been important subjects for science and policy in the UK since the United Nations Conference on the Human Environment 40 years ago (Sweden, 1971). The development of strategies to reduce the effects of transboundary pollution on human health and ecosystems has evolved along with scientific understanding of the subject over this period. This review follows a detailed analysis of the subject at the turn of the new millennium (NEGTAP, 2001) which included monitoring up to 1997. This review takes place 20 years since countrywide UK monitoring networks were established in 1986 to quantify the concentrations, deposition and countrywide budgets of the key pollutants, and following large reductions in emissions of some of the most important contributors to the transboundary exchange of pollutants. The data now available provide a time series twice as long as that available for the NEGTAP review and, while not comprehensive, they provide the best picture available to date of the way in which the chemical composition of the atmosphere over the UK has responded to changes in emissions. Ecological effects research and monitoring of the UK environment during this period of significant change in emissions provide evidence of the responses of ecosystems to changes in pollutant exposure, and identifies the main chemical species responsible and their sources.

An important feature of the current report is its focus on what has changed in the UK environment since the detailed review by NEGTAP. This review differs from the earlier one in not describing all the background mechanistic science; for this material the reader is referred to the earlier report and associated literature. Instead, it focuses on the degree to which changes in emissions have led to changes in the concentrations and deposition of pollutants and in their effects on ecosystems throughout the UK. Within each of the chapters available data are used to illustrate the main changes detected, but given the quantity of monitoring data available the reader is referred to online sources of wider data holdings. In this way the science presented includes the entire scope of study from emissions, atmospheric concentrations and deposition, and long-range transport and deposition modelling, to effects on vegetation, soil and freshwaters, and discusses the wider geographical context of transboundary pollution issues in Europe within a concise report. The review considers the primary pollutants sulphur dioxide (SO_2), nitric oxide (NO) and nitrogen dioxide (NO_2), ammonia (NH_3), volatile organic compounds (VOCs) and, for the first time, heavy metals (lead, cadmium, mercury, zinc, copper, nickel and arsenic), and reaction products of their interactions in the atmosphere.

The international legislation to control long-range transport of pollutants in Europe is summarised in Table 1.1. The most important legislation for the UK in this field is currently the United Nations Economic Commission for Europe (UNECE) Gothenburg Protocol (1999), currently under review (LRTAP, 2007), and the European Union National Emission Ceilings Directive (NECD) (CEC, 2001b).

Table 1.1: International pollutant emission control protocols within the United Nations Economic Commission for Europe (UNECE).

Protocol	Open for signature	Entry into force*	Environmental effect	Number of signatures (as of 17th Dec 2008)**	Number of ratifications (as of 17th Dec 2008)**
Acidification, Eutrophication and Ground-level Ozone (Gothenburg)	1999	2005	Acidification, eutrophication and ground-level ozone	31	25
Persistent Organic Pollutants (POPs)***	1998	2003	Accumulation of POPs in the environment	36	29
Heavy Metals	1998	2003	Accumulation of heavy metals in the environment	36	29
Further Reduction of Sulphur Emissions	1994	1998	Acidification	28	28
Volatile Organic Compounds	1991	1997	Summer smog (ground-level ozone)	25	32
Nitrogen Oxides	1988	1991	Acidification, summer smog (ground-level ozone)	19	23
Thirty per cent Reduction in Sulphur Emissions	1985	1987	Acidification	19	21
European Monitoring and Evaluation Programme (EMEP)	1984	1988	Long-term financing of EMEP	22	42
Convention on Long-range Transboundary Air Pollution (CLRTAP)	1979	1983	Framework for controlling and reducing the damage to human health and the environment caused by transboundary air pollution	32	51

*Sixteen ratifications are needed for a protocol to enter into force
**Updated status can be found at http://www.unece.org/env/lrtap/
***POPs will not be considered further in this report

The target reductions in pollutant emissions for the UK from the Gothenburg Protocol and from the NECD represent important policy goals. The expected reductions in exposure and effects following reductions in emissions are important foci for this review, showing the degree to which expected improvements in environmental quality have been delivered by policy actions.

Chapter 2 Emissions

Summary

- Substantial reductions in emissions of most pollutants have been achieved over the last three decades. There have been substantial reductions from industry due to effective monitoring and control, and decreases from combustion sources in general caused by fuel switching to natural gas. Note that emissions of heavy metals are covered in Chapter 6.
- Emissions of sulphur dioxide decreased by 94% between 1970 and 2010. The UK met the EU National Emissions Ceilings Directive (NECD) target for 2010, with emissions 31% below the target value.
- Emissions of nitrogen oxides (NO_x) decreased by 58% between 1970 and 2010. Emissions in recent years had not been reduced by as much as originally anticipated by policy makers, possibly because emissions from new diesel vehicles had not decreased under real world conditions in line with emissions measured during regulatory test cycles. However, the latest emission data show that the UK met the NECD target for 2010, with emissions 5% below the target value.
- Verification studies show divergence of trends between roadside concentrations and road transport emissions of NO_x. It is suspected that this is caused by underestimation of the emissions inventory for recent years, but this has not yet been established.
- Emissions of ammonia have decreased by 21% between 1990 and 2010. The UK met the NECD target for 2010, with emissions 4% below the target value.
- Emissions of non-methane volatile organic compounds (NMVOCs) have decreased by 61% between 1970 and 2010. The UK met the NECD target for 2010, with emissions 34% below the target value.
- Policies to tackle greenhouse gas emissions have the potential to affect emissions of air quality pollutants. Most policies should reduce emissions of air quality pollutants, but some may give rise to increases. Examples include the increased use of biomass, or carbon capture and storage in electricity generation.

2.1 Introduction

The following sections consider the current knowledge on emissions in the UK for sulphur dioxide (SO_2), nitrogen oxides (NO_x), ammonia (NH_3) and non-methane volatile organic compounds (NMVOCs). A number of different aspects are considered for each pollutant:

- Historic trends are presented and the major sources are considered in turn.
- Projected emission estimates are shown and discussed in terms of compliance with targets from international legislation.
- Emission maps are provided and spatial distributions are explained.
- The levels of uncertainty associated with the emission estimates are discussed.
- Information on verification studies is presented where available.
- Where possible, comments are made regarding potential links to and dependencies on climate change.

2.2 Sulphur

2.2.1 Overview

Air emissions of sulphur (S) primarily arise from fuel combustion and the release of the sulphur which naturally occurs in trace quantities in fossil fuels. Emissions from coal combustion dominate the national totals across Europe, and in 2008 solid fuels accounted for 55% of the UK total sulphur emission. UK emissions in 2010 were 203 Gg-S, (Defra, 2011).

The most common methodology to estimate S emissions uses a 'life cycle' approach. It is assumed that all of the S in the fuel is emitted to air as sulphur dioxide (SO_2), with the exception of the S remaining in any ash or residues (EMEP/EEA, 2009).[1] Some large sources employ sulphur abatement equipment and provide plant-specific emissions which are incorporated into the UK emissions inventory.

Across the last several decades the UK Government has introduced a range of measures to reduce S emissions from large combustion installations. The 2010 emission figures confirmed that the UK exceeded the NECD target of 293 Gg-S by 31% (CEC,2001b; Defra, 2011).

2.2.2 SO_2 emission trends

Figure 2.1 below shows trends in UK emissions of SO_2. Since 1970 there has been a substantial reduction in emissions from most sources.

Declining heavy industry

From the late 1970s through to the 1990s the UK underwent a change from an economy dominated by manufacturing to a service-based economy. As a result there were substantial reductions in the levels of heavy industry in the UK, most notably in the iron and steel sector (DECC, 2009). This gives rise to the emission reductions observed in the early part of the timeline shown in Figure 2.1.

Increased use of gas in electricity production

Emissions from the electricity generating sector are relatively constant across the first half of the timeline shown in Figure 2.1. Variations in the observed trend are typically an indication of cold or mild winters. However, substantial reductions are seen from the early 1990s onwards. These reductions occurred because there was significant fuel switching from coal to gas in the domestic, industrial and electricity generating sectors. S emissions from the electricity generating sector are shown in more detail in Figure 2.2, with the fuel mix used for electricity generation shown in Figure 2.3.

The driver for fuel switching was economic, gas being a cheaper alternative for domestic users and modern CCGT (combined cycle gas turbine) gas-fired power stations providing improved efficiencies compared to older technologies. In 1992 the use of gas was

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[1] In the emissions inventory field, it is usual to express sulphur emissions as SO_2. However, to ensure consistency with other chapters in this report, the emissions are quoted as mass of S, and care should therefore be taken when comparing figures presented here with any other published emissions data.

responsible for only 2% of electricity generation, but by 2000 this had grown to 34%. Conversely, the contribution from coal fell from 61% to 35% over the same time period (DECC, 2009).

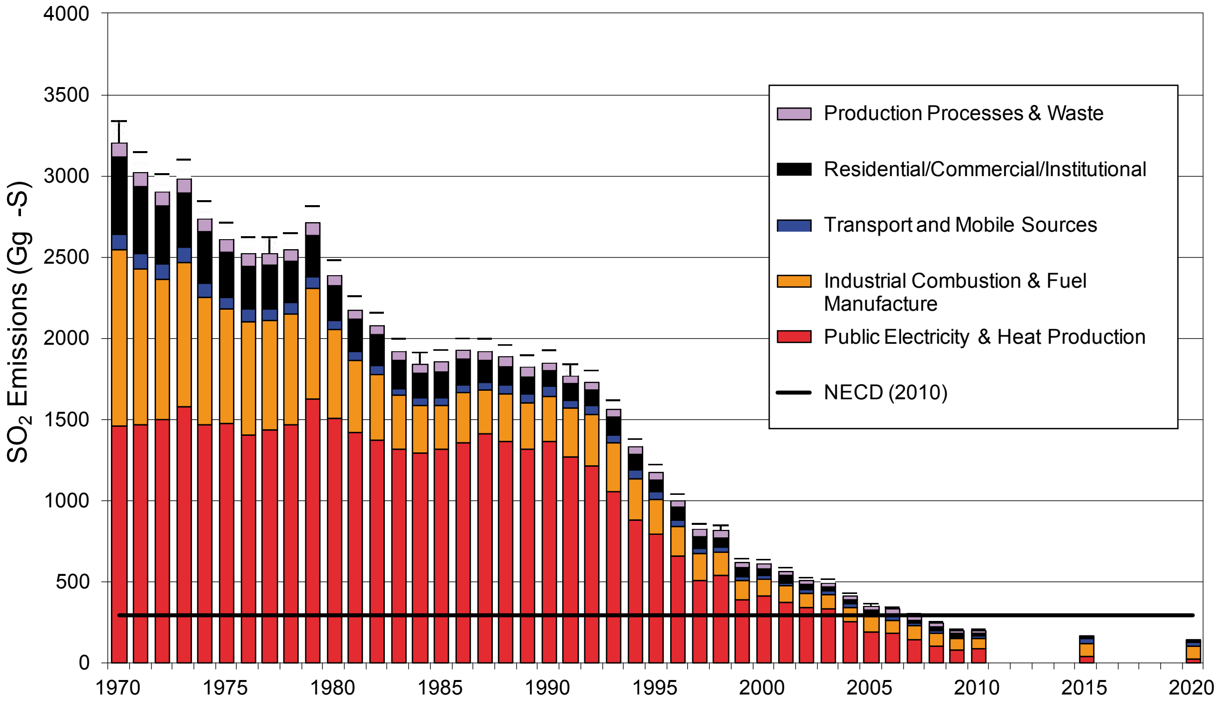

Figure 2.1: UK emissions of sulphur dioxide (Defra, 2011; EIONET 2012) (Gg-S)[2].

Since 2000, changes in fuel prices have meant that coal has become more attractive for electricity generation, and consumption increased in a number of years. However, emissions of S still show a steady decline. This is due to legislation associated with restricting S emissions from large combustion plant, which has resulted in the installation and use of emissions abatement equipment. Flue gas desulphurisation abatement equipment is highly effective at removing S from stack emissions, and its use has ensured that emissions have continued to fall, even though coal use has increased since 2000.

The increased use of oil in 1984 (and 1985) at the expense of coal was due to the miners strike.

Control of industrial emissions

The UK Government has a long track record of ensuring that emissions from large sources are monitored and controlled. The Environmental Protection Act 1990 established a system of 'Integrated Pollution Control' (IPC) to monitor emissions from industrial installations.

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[2] The projections used here are based on the UEP38 energy scenario.

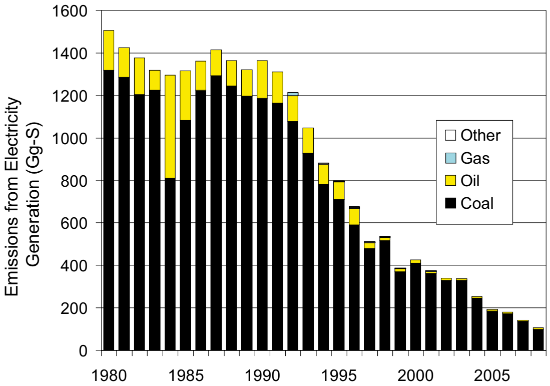

Figure 2.2: Sulphur emissions from electricity generation by fuel (Gg-S) (Data taken from CEIP (2010)).

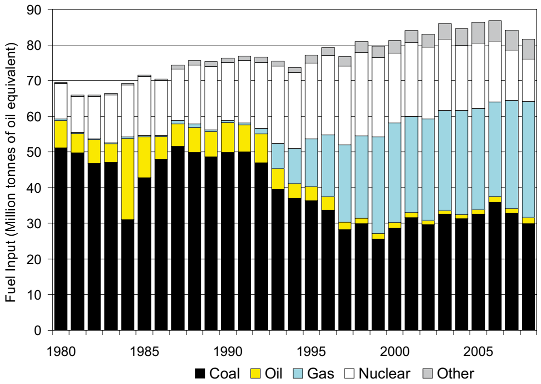

Figure 2.3: Fuel mix used for electricity generation in the UK (Data taken from DECC (2009)).

In 1996 the European Union adopted Directive 96/61/EC which was concerned with integrated pollution prevention and control (‘the IPPC Directive’). In short, this Directive requires large industrial installations to have a permit before they can be operated, the permit scheme in the UK being controlled by the Environment Agency, the Scottish Environment Protection Agency and the Northern Ireland Environment Agency.

In 1997 the Large Combustion Plant Directive (CEC, 2001a) was introduced to control emissions specifically from power stations.

All of this national and international legislation has targeted the control of S emissions (as well as many other pollutants) from industry, and has played a key role in ensuring the continued decrease of S emissions in the UK.

The domestic sector

Smoke Control Areas, implemented by local authorities, have restricted the use of coal in more densely populated urban areas since the 1950s (see http://www.uksmokecontrolareas.co.uk/#legi). However, the observed national decreases in emissions across the timeline (Figure 2.1) are primarily caused by a number of additional factors.

In the late 1980s the natural gas mains network spread from urban centres to surrounding areas of lower population density, making gas increasingly available to a large cross-section of the domestic sector. The availability of gas, as a more financially attractive option, resulted in the gradual displacement of domestic coal and oil use (DECC, 2009). The impact was further enhanced by the general availability of more modern heating systems (both gas and electric), which offered a more convenient and efficient alternative to coal.

More recently, reduced emissions from the domestic sector have been the result of general improvements in building standards, increased use of home insulation and general public awareness. These changes have come about through the drive to decrease greenhouse gas emissions by reducing fuel consumption.

The impact of all of these changes has resulted in a substantial reduction in total S emissions across the timeline shown in Figure 2.1. Emissions have fallen from 3213 Gg-S in 1970 to 203 Gg-S in 2010, representing a 94% reduction (Defra, 2011).

Sulphur emissions from shipping

Increased reduction and control of S emissions from the major source sectors means that some sources which previously contributed a small amount to the national total have, or will, become more significant. 'National' shipping emissions are a small component of the UK S emissions presented above (3% of the UK total in 2010), despite the fact that fuel with a relatively high S content is currently used. However 'international' shipping is not included in reported national totals (it is not included in Figure 2.1) and is a larger source. Activity levels of shipping in general have been increasing with time as other sources have been significantly reduced. As a result, current trends suggest that shipping is set to become one of the most important contributors to UK S deposition in future years, particularly in coastal areas (see Figure 2.4). S deposition from shipping is further considered in Chapter 4 (Section 4.2).

The international nature of shipping has made it difficult to co-ordinate efforts to introduce legislation to control emissions. However, MARPOL Annex VI entered into force in 2005 (MARPOL, 1997) and sets limits on S (and nitrogen oxides (NO_x)) emissions from ship exhausts. Annex VI sets a global cap of 4.5% by mass on the S content of fuel oil. In addition, it includes provisions allowing for special 'SO_x Emission Control Areas' (SECAs)

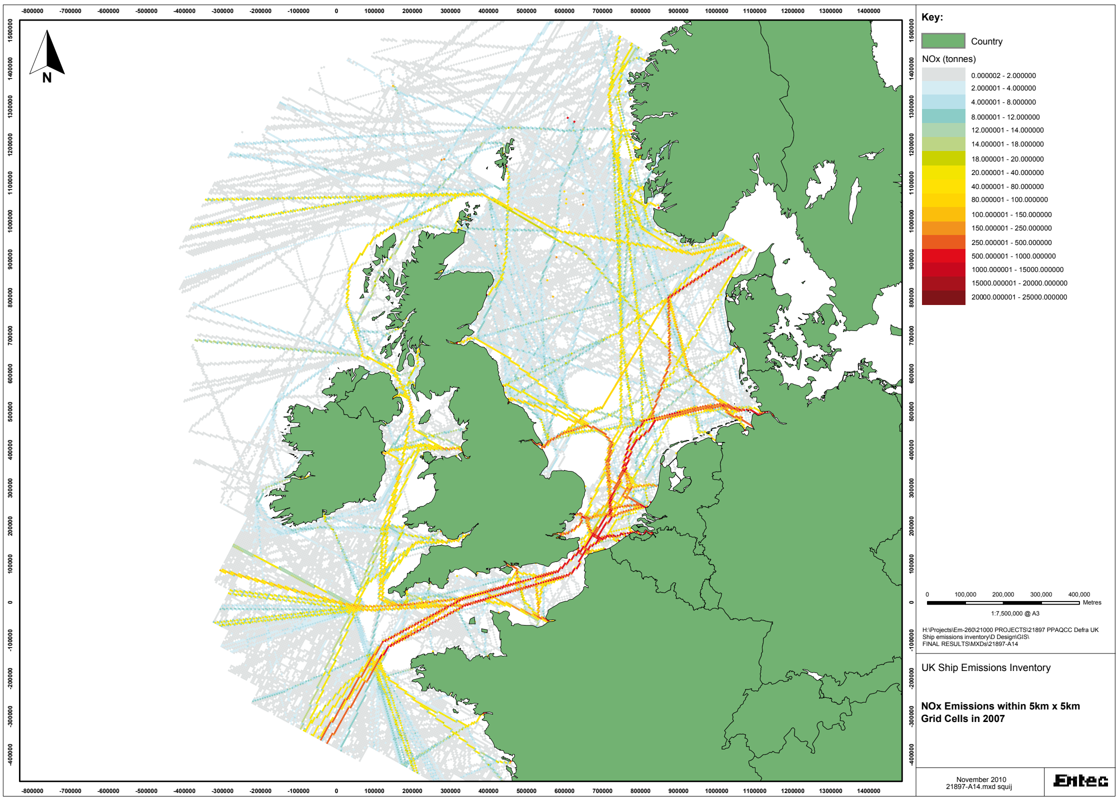

Figure 2.4: Sulphur emissions (expressed as tonnes SO_2) from UK and international shipping in 2007 (Whall *et al.*, 2008).

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to be established where the sulphur content of fuel oil must not exceed 1.5% by mass (or ships must employ emissions abatement equipment). The North Sea and English Channel have been defined as SECAs. As a result, shipping using these areas has been required to use low S fuel since 22nd November 2007.

It is not yet clear to what extent this legislation will lead to real world reductions in SO_2 emissions. It is understood that providing enough low S fuel has been a challenge for oil refineries. The alternative, installation of abatement equipment, can have practical difficulties and has a significant lead time. Despite this, current projections indicate that the Annex VI legislation will give rise to at least 85% reductions in the 2020 SO_2 emissions from shipping in the vicinity of the UK. Recognising the importance of this source for the modelling community, work has been undertaken to significantly improve the emission estimates from shipping. Mapped emissions from all shipping are now available (Figure 2.4).

2.2.3 Sulphur emission projections and progress towards targets

UK emissions projections are compiled for a number of pollutants. The methodology uses a number of different datasets. In summary:

- BIS energy forecasts are used to determine future fuel consumption by fuel type and by sector.
- Economic growth forecasts are used to project the changing activity levels of some source sectors.
- Data from the Department for Transport are used to project both the levels of traffic growth and the changes to the vehicle fleet.
- Expert judgement is used to assess changes in plant operating efficiencies, installation of abatement equipment, the penetration of new technologies and other changes to operating practices which might change emission rates.
- Legislation and Government policies which are in place, or are scheduled to be introduced, are also taken into account.

A more comprehensive explanation of the methodology may be found in Wagner et al. (2009).

The UK is a signatory to the Gothenburg Protocol (UNECE, 1999). This commits the UK to reducing emissions of S to 625 Gg-SO_2 (313 Gg-S) by 2010. In addition, the UK is also a signatory to the EU National Emission Ceilings Directive (CEC, 2001b), which requires 2010 emissions of SO_2 to be 585 Gg (293 Gg-S) or lower.

Figure 2.1 includes the more stringent target under the NECD and shows that the UK achieved the NECD ceiling in 2010; exceeding the target by 31% (Defra, 2011). The projected emission estimates show similar trends to those evident from the historic emissions explained above. The most significant emission reductions are projected to be from the electricity generating sector and industrial sources. The Industrial Emissions Directive is currently being debated within the EU, and will set tighter emission limits for power plant, including gas plant; this will result in a further significant reduction in emissions from the sector by 2020. In addition, both the Gothenburg Protocol and the NECD are shortly to be reviewed, and new emission ceilings for 2020 are expected to be established. The revised emission ceilings are likely to shape future Government policy on emissions control.

2.2.4 Spatial distribution of SO_2 emissions

Figure 2.5 shows the UK SO_2 emissions mapped at a 1 km x 1 km resolution. SO_2 emissions are dominated by large industrial sources which are mapped as points. As a result, the majority of the UK total emission occurs in only a few individual grid cells, which is difficult to see on the emission map. Transects across the S emissions map therefore give wide variations in emissions when compared to other pollutants (which have a larger contribution from area sources and less variability from grid cell to grid cell).

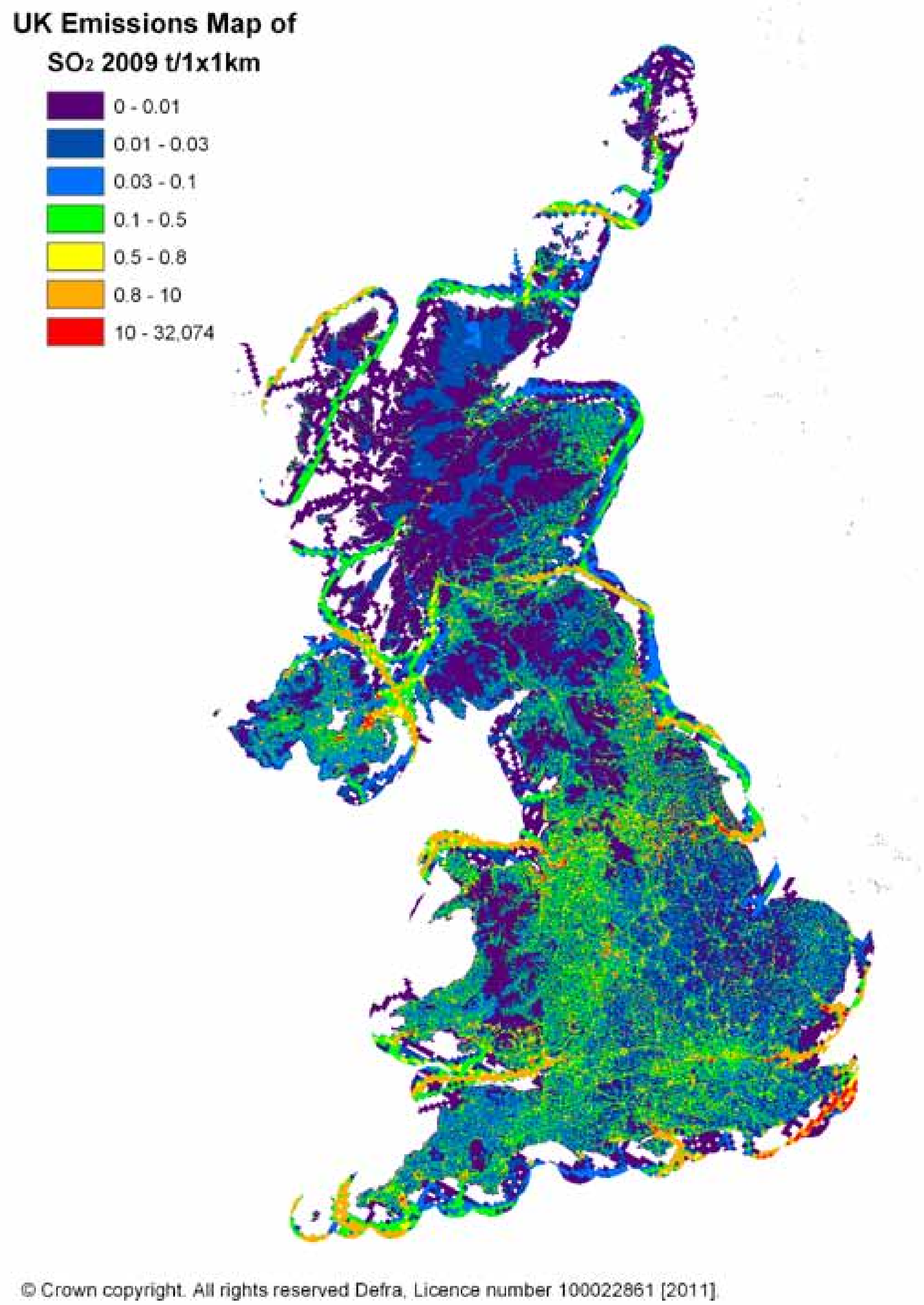

Figure 2.5: Mapped emissions of SO_2 (expressed as tonnes SO_2) (NAEI, 2011).

The spatial pattern which can be observed on the map represents the emissions from small industrial installations. There is also a smaller contribution from road transport and the domestic sector.

The dominance of large point sources has an important impact on the dispersion of S emissions. As the majority of emissions are released from large point sources, they are released from a high stack under conditions of good atmospheric dispersion. This promotes effective dispersion and avoids major impacts of SO_2 close to the stack at the ground level.

Emissions from UK shipping in territorial waters are included in Figure 2.5, with higher emissions per grid cell evident close to major ports. Including only UK territorial emissions allows the map to be consistent with an overall UK emissions total. However, as mentioned in Section 2.2.2, modellers use shipping emissions over a larger area as input into their models, as shown, for example, in Figure 2.4.

2.2.5 Uncertainties in sulphur emissions

The emissions in Figure 2.1 are shown with error bars, which represent a 95% confidence interval of ±3% of the total annual emission. This uncertainty in S emissions has been determined by conducting a Monte-Carlo analysis of uncertainties (Murrells *et al.*, 2010).

The two most significant sources of uncertainty in the emission estimates are the quantities of fuel consumed and the S content of those fuels. However, the majority of S emission estimates are available on a site-by-site basis. This is because large industrial installations are required to report their emissions and demonstrate that these are lower than their emission permits. Operators therefore closely monitor S emissions to ensure compliance.

Emissions from international and domestic shipping are considerably less well characterised. This is because the fuel is sourced from different countries, making it difficult to assess total fuel consumption. Emission estimates based on ship movements also carry a significant uncertainty in assessing a fuel consumption estimate.

Uncertainty estimates have also been made for projected emissions of S, and are ±6% for 2010, increasing slightly for 2015 and 2020 (Wagner *et al.*, 2009). The calculation requires expert judgement, thus increasing the overall uncertainty in emissions.

Uncertainties in spatial distribution

The dominance of point sources means that the majority of S emissions are considered to be well mapped. However, the smaller area sources, such as mobile machinery, are difficult to spatially disaggregate in a reliable manner.

2.2.6 Climate change

Emissions of SO_2 are reported as an ‘indirect greenhouse gas’ under international reporting requirements associated with climate change, because they contribute to aerosol formation and to cooling of the climate system. Emissions of S are not expected to be greatly influenced by the effects of climate change itself. But, the implementation of policy relating to climate change is expected to introduce changes to fossil fuel consumption, which will have the direct effect of reducing emissions of S (EEA, 2006).

However, it is expected that future emissions controls and targets for SO_2 will be determined by both the observed levels of acidification across Europe and the impacts on human health from particulates, rather than climate change (European Commission, 2008). Control of sulphur emissions will add to global warming as aerosols and their cooling influence are removed from the atmosphere.

2.3 Nitrogen dioxides (NO_x)

2.3.1 Overview

Air emissions of nitrogen oxides (NO_x) primarily arise from combustion sources. The nitrogen (N) that is oxidised to NO_x during combustion can come from the fuel or the air, depending on combustion conditions and fuel type.

Emissions from road transport currently make the largest contribution to the UK total, accounting for some 33% in 2010 (Defra, 2011). The methodology for estimating NO_x emissions from most sources is complex because road transport comprises varied sources within the sector. The estimation methodology therefore needs to be particularly sophisticated to account for the large number of parameters which influence NO_x emissions. Extensive measurement programmes are conducted to assess exhaust emissions from different vehicle types and a number of emission models are currently available. The UK National Atmospheric Emissions Inventory (NAEI) uses a detailed model using UK-specific activity data and assumptions relating to the emissions performance of vehicles in the UK fleet to make estimates of emissions from road transport (Murrells *et al.*, 2010). The model is based on established methodologies recommended in the EMEP/EEA Emissions Inventory Guidebook (EMEP/EEA, 2009) using speed-related emission factors for different vehicle types, engine sizes, fuel types and Euro emission standards, combined with activity data on traffic, speeds, vehicle age and fleet composition based on Department for Transport statistics.

The public electricity and heat generation sector accounted for 25% of NO_x emissions in 2008 (CEIP, 2010). Large combustion sources are required to report annual emissions of NO_x, and ensure that emissions do not exceed specified limits. Consequently plant operators use monitoring programmes to assess their emissions.

The UK met the NECD target with the 2010 emissions 5% below the target value of 359 Gg-N (CEC, 2001b; Defra, 2011).

2.3.2 NO_X emission trends

Figure 2.6 presents a time series of NO_x-N emissions.[3] Significant reductions are evident from 1990 onwards.

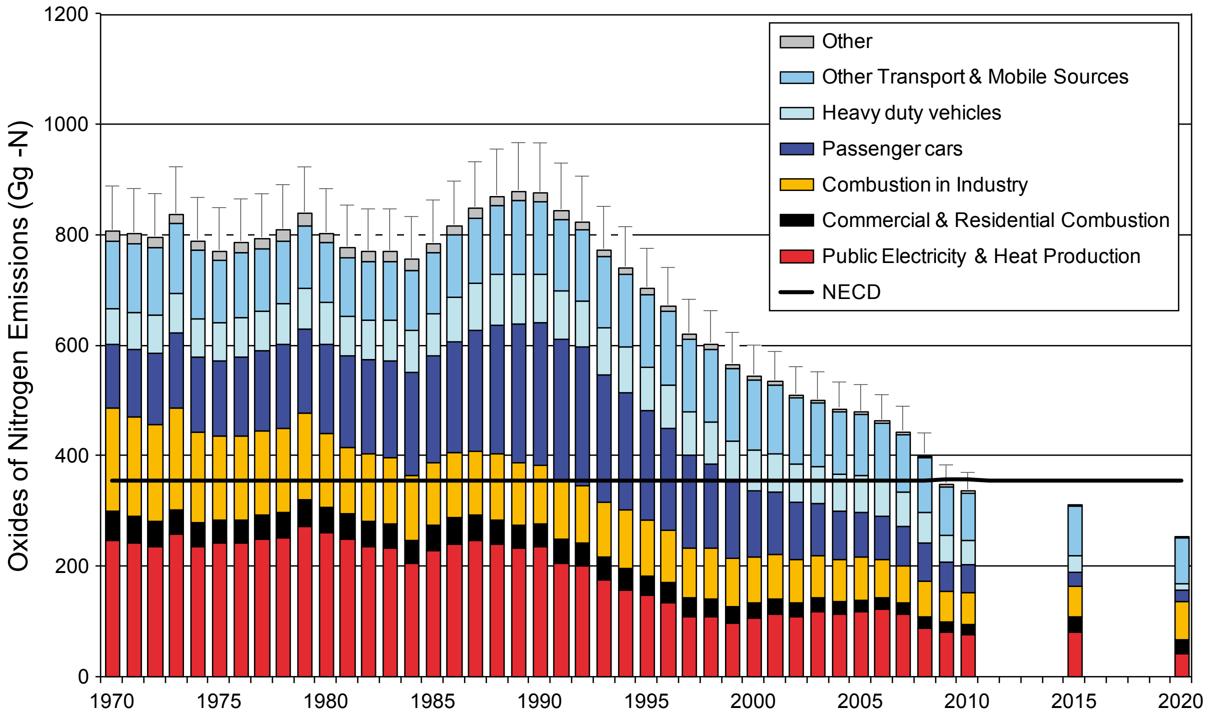

Figure 2.6: UK emissions of NOx-N (Gg-N) (Defra, 2011; EIONET 2012)[4].

Emissions from electricity generation

NO_x emissions from electricity generation (Figure 2.6) are fairly constant across the first portion of the time series until 1990. Variations are caused by very cold or mild winters, or changes to the fuel mix used for electricity generation. An example is the decreased emissions which can be observed in 1984. This was the year of the coal miners strike when there was a large reduction in the amount of coal used for electricity generation, and a corresponding increase in use of oil. This is also shown in Figure 2.3.

During the early 1990s the increased use of gas in electricity generation displaced coal and oil (DECC, 2009). The cleaner fuel and more modern power stations led to a significant reduction in NO_x emissions from the sector until 2000. From 2000, the absolute level of gas used for electricity generation remained fairly constant, and increased demand was met by coal-fired power stations. This meant that NO_x emissions from the electricity

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[3] In the emission inventory field, it is usual to express NO_x as a mass of nitrogen dioxide (NO_2). However, to ensure consistency with other chapters in this report, the emissions are quoted as mass of N in the NO_x (NO_x-N), and care should therefore be taken when comparing figures presented here with any other published emissions data.

[4] The projections used here are based on the UEP38 energy scenario.

generating sector increased. More stringent abatement of emissions from the electricity generating sector was considered (e.g. the installation of selective catalytic reduction, SCR), but assessments indicated that it was not the most cost-effective option. Since 2006, coal use (and the total amount of fuel used in electricity generation) has substantially decreased (DECC, 2009).

NO_x emissions from road transport

The road transport sector has provided a significant contribution to the downward trend in UK emissions. The emissions of NO_x from road transport are shown in more detail in Figure 2.7 below.

The first petrol cars with three-way catalysts were introduced in 1992, and this resulted in a significant reduction in NO_x emissions. In subsequent years new, more stringent emission standards have been introduced for petrol cars sold in Europe.

Emission limits for diesel cars and light goods vehicles came into effect in 1993/94. Limits on emissions from heavy goods vehicles (HGVs) first came into effect in 1988 leading to a gradual reduction in emission rates as new HGVs penetrated the fleet. More stringent emission limits were introduced for HGVs in 1993/94, further contributing to the decrease in emissions (CEIP, 2010).

The introduction of these standards has had a substantial impact on NO_x emissions from the road transport sector. However, some trends have given rise to emission increases. For example, the UK consumption of petrol peaked in 1990 and since then has been

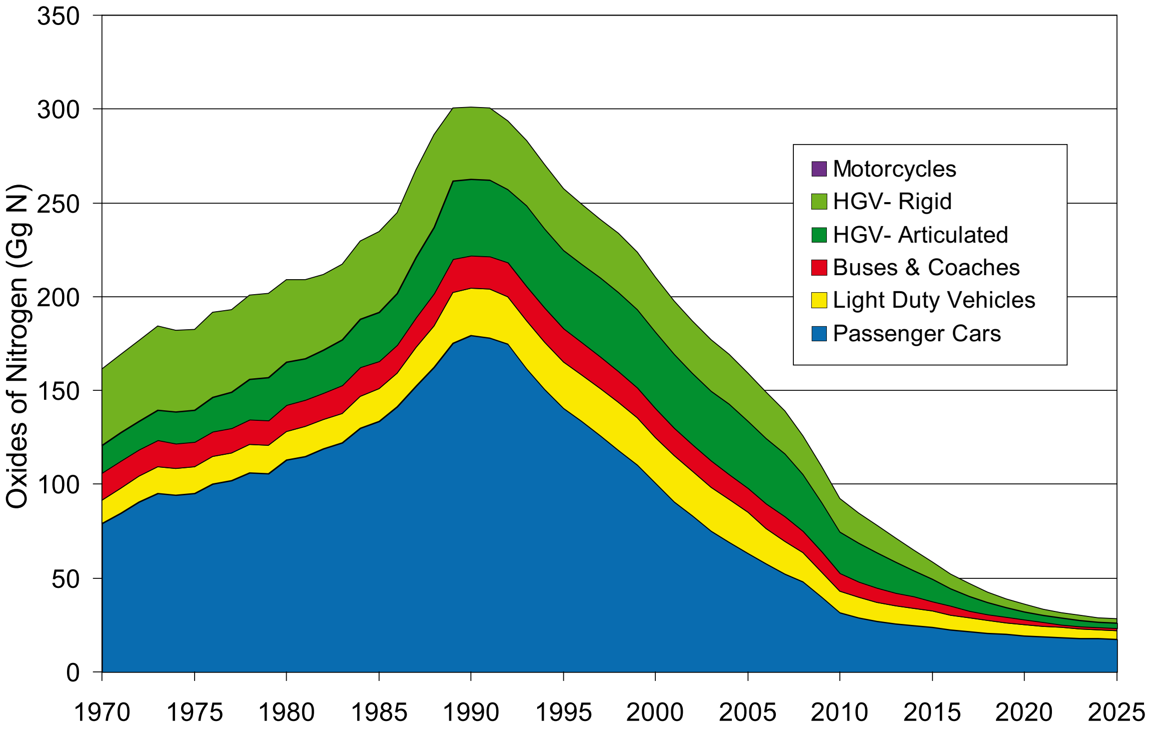

Figure 2.7: Emissions of NO_x-N (Gg-N) from road transport by vehicle type (CEIP, 2010).

declining by approximately 2% per annum. Conversely, diesel consumption has shown a steady growth (approximately 8% per annum) over the same period (DECC, 2009). Diesel vehicles emit more NO_x per km than their petrol equivalents.

Primary NO_2 emissions

One issue which has become apparent in recent years is that, whilst the more modern vehicle fleet has delivered reductions in NO_x, this has not resulted in a similar reduction in nitrogen dioxide (NO_2). This is of particular concern because it is NO_2 which impacts on human health, and the UK Government set limit values for NO_2 concentrations to be achieved by 2010.

It has generally been assumed that 5% of NO_x is emitted as primary NO_2, and the conversion of nitric oxide (NO) to NO_2 in urban areas is known to be limited by the available oxidant (AQEG, 2007b). The reason why urban NO_2 concentrations have not decreased as rapidly as NO_x is partly because of an increase in the proportion of NO_x emitted as NO_2 from modern diesel vehicles. First, there has been an increase in the use of diesel vehicles (DfT, 2009) and combustion conditions in a diesel engine are favourable for NO_2 formation. Furthermore, some after-treatment technologies (e.g. oxidation catalysts and continually regenerated diesel particulate traps) are thought to lead to increased emissions of primary NO_2 (Murrells *et al.*, 2010).

Modelling studies show that roadside concentrations of NO_2 are currently expected to exceed 2010 limit values set by the European Commission in a large number of urban locations across the UK (Stedman and Grice, 2009). As a result, the UK Government has applied for a time extension notification. This will then allow enough time to put in place a number of different measures to reduce emissions from the road transport sector, and hence roadside NO_2 concentrations, to acceptable levels by 2015.

London emissions validation study

A study to compare the output from the London Atmospheric Emissions Inventory (LAEI) with NAEI emission estimates has been reported (Bush and Griffin, 2008a; Bush and Griffin, 2008b; Bush and Tsagatakis, 2007). This was done by creating a subset of NAEI emission data (from the emission maps) which corresponded to the London area in the LAEI. The purpose of the study was to investigate whether the NAEI was underestimating emissions in London, to identify differences in methodology and input data, and to assess where improvements could be made in either emissions inventory.

For many sources the comparison was complicated by difficulties in comparing like with like. In particular it should be noted that the most up-to-date version of the London inventory at this time was for 2004. NAEI emission maps are only created for the most recent year. As a result the 2004 NAEI emission map was already two years out of date when the LAEI comparison study was conducted, being superseded by NAEI maps for later years which had incorporated a wide range of improvements. It is also important to appreciate that the NAEI dataset was generated from the UK emission maps (i.e. 'top-down' rather than the standard 'bottom-up' inventory compilation). The NAEI dataset therefore relies on the accuracy of both the UK-level emission estimates and the spatial distributions from the UK emission maps. Despite these difficulties, it was possible to compare whether the two datasets gave similar results, and investigate the source of any significant differences.

A comparison of hot exhaust emissions for NO_x showed that the NAEI estimate was 33% higher than the LAEI. Analysis of the input data and underlying assumptions indicated that the major differences in the calculation methodologies were:

- The LAEI includes a London-specific taxi and bus fleet. The NAEI maps at the time did not distinguish between cars and taxis.
- The taxi and bus fleet in the LAEI is cleaner and more fuel efficient than the car and bus fleet in the NAEI.
- Vehicle speeds in the LAEI are generally higher than those in the NAEI.
- Estimates of fuel consumed by road traffic in the NAEI are higher than those in the LAEI.

Since the comparison, a number of improvements have been made to the NAEI emission estimates to incorporate the localised data available from the LAEI. In addition, improvements have also been made to the LAEI.

Verification of the NO_x trends reported in the NAEI

It is important to understand whether the road transport NO_x emission inventories adequately reflect real world behaviour and whether ambient levels of NO_x have been

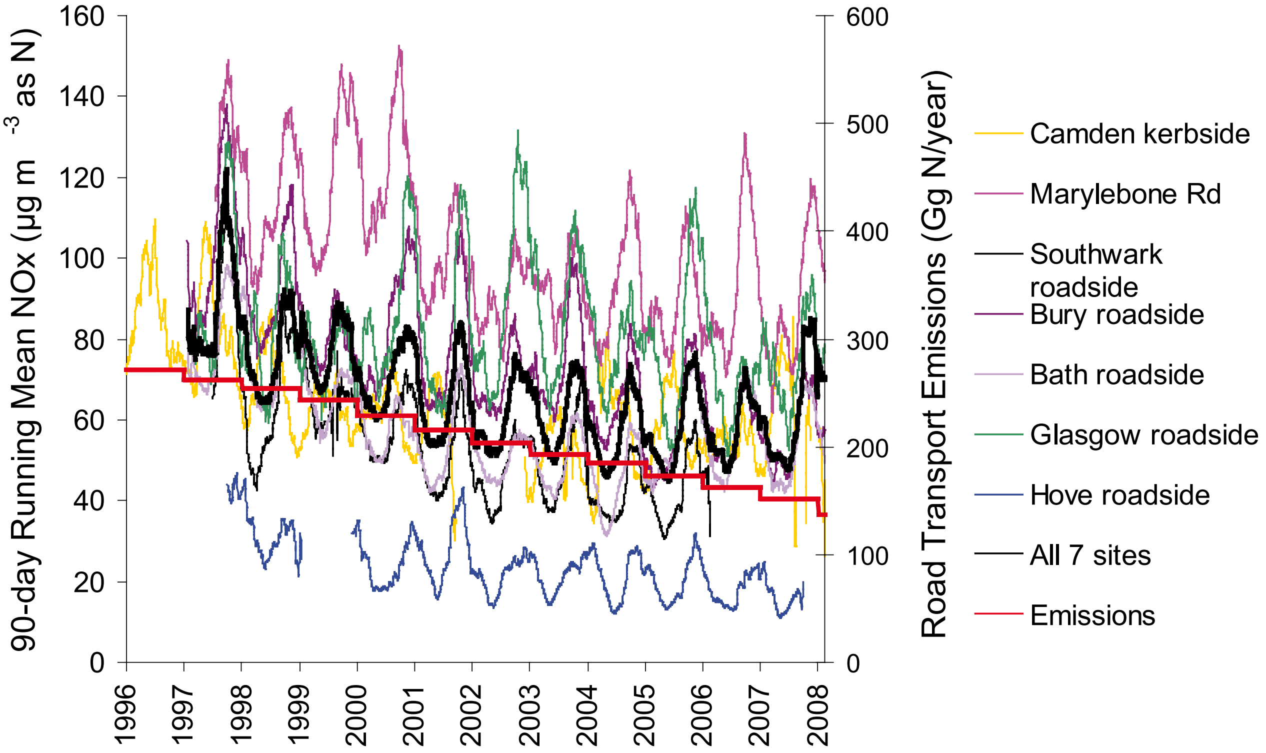

Figure 2.8: Roadside NOx-N concentrations and NAEI NOx-N road transport emissions comparison. Derived from ratified AURN data (http://www.airquality.co.uk) and NAEI emissions data (Murrells et al., 2010).

reduced accordingly. Figure 2.8 presents the observed trends in NO_x concentrations, as 90-day rolling mean concentrations, for seven roadside and kerbside locations in the UK over the period 1996–2008. UK road transport NO_x emissions from the NAEI have been over-plotted for the same period.

The agreement in shape between the observed roadside and kerbside NO_x concentrations and the UK road transport NO_x emissions is striking, at least until the end of 2005. The average concentration at the seven sites shows an annual decline of about 3.6% per year and the emission inventories a slightly greater annual decline of about 4.7% per year. This general agreement shows that the assumptions made concerning the take-up and performance of three-way catalysts in petrol-engined passenger cars and of diesel emission control technologies reflect real world behaviour.

However, there is a noticeable change in the observed NO_x concentration trend from 2006 onwards, with the decrease changing to a slight increase. In contrast, emission estimates show a continued decrease. Whilst the increased concentrations may be caused by unusual meteorological conditions, this seems unlikely across the three years of data that are available. It is more likely that the NAEI is underestimating emissions from the more modern vehicles in the fleet, resulting in the divergence of the emissions and concentration trends with time. As a consequence, it is likely that projected NO_2 concentrations may not reach acceptable air quality targets and guidelines in the foreseeable future.

2.3.3 NO_x emission projections and progress towards targets

UK emission projections are compiled for NO_x; some brief comments on the approach taken have been included in Section 2.2.3 and more detail may be found in Wagner *et al.* (2009).

The UK is a signatory to the Gothenburg Protocol (1999). This committed the UK to reduce emissions of NO_x to 1181 Gg of NO_x as NO_2 (359 Gg-N) by 2010. In addition, the UK is also a signatory to the EU National Emission Ceilings Directive (NECD) (CEC, 2001b), and chose to agree more stringent emission targets than those under the Gothenburg Protocol. Under the NECD, the UK was required to decrease emissions of NO_x to 1167 Gg of NO_x as NO_2 (355 Gg-N) by 2010. Modelling studies at the time showed that the UK would reach this target without needing to apply any additional measures beyond those which were known to be coming into force, relating to control of industrial and road transport emissions (Holland *et al.*, 2000).

Figure 2.6 includes the more stringent target under the NECD, and shows that the emissions of NO_x reported for 2010 were 5% below the NECD target value of 359 Gg-N.

Historically, emission targets have been expressed as percentage reductions. However, fixed ceilings are now being used because modelling studies at the European level can determine the absolute emissions from countries at which concentrations or deposition of pollutants are reduced to acceptable levels. So the ceilings set can be directly related to specific improvement to either ecosystems or human health.

More modern vehicles (Euro 5/V onwards) are required to perform to tighter emission standards. However, recent evidence from roadside and other 'real world' tests suggests that modern diesel vehicles may not be delivering the reduction in NO_x emissions required by the legislation (Ligterink *et al.*, 2009). Further examination of emission factors under real world conditions is required which might lead to an increase in the NO_x emission factors currently assumed in inventories for Euro 5/V diesel vehicles.

The economic downturn is expected to have an impact on future emissions. Whilst it may be expected that people will choose to drive less, it is also true that the sales of new, cleaner vehicles will substantially decrease. In terms of emissions reduction, the relative importance of these two factors is expected to depend on the vehicle type.

As mentioned in Section 2.2.3, both the Gothenburg Protocol and the EU NECD are expected to be updated soon, and a new NO_x ceiling for 2020 is expected. In addition the Industrial Emissions Directive will introduce more stringent emission standards for the electricity generating sector. One interesting observation regarding the projected emissions of NO_x is that the balance of high and low level sources will remain broadly similar. Whilst emissions from road transport will decrease more than other sources, by 2020 the high and low level sources will contribute approximately half each to the national total.

2.3.4 Spatial distribution of NO_x emissions

Figure 2.9 shows the UK NO_x emissions mapped at a 1 km x 1 km resolution. The most prominent features on the map are the emissions from the road transport sector. This is because emissions of NO_x per km increase with vehicle speed. As a result the major road network (with both high vehicle speeds and high traffic flows) can easily be picked out as giving high emissions. In addition, larger diesel vehicles, which are responsible for a significant portion of total NO_x emissions, spend more time on the major roads. The non-motorway roads are also clearly visible. Urban centres show as hot spots, due to the high density of traffic emissions and the smaller contribution from the residential and commercial sectors, as well as other area sources such as mobile machinery.

Emissions from electricity generation and large industrial installations are not easily visible as they are concentrated in individual grid cells. Clusters of point sources can be seen off the east coast of Norfolk and further north. These represent emissions from individual offshore oil and gas platforms. Emissions from UK shipping in territorial waters are also included and distributed according to the most recently available studies (Whall et al., 2008).

2.3.5 Uncertainties in NO_x emissions

As previously mentioned, NO_x emissions depend on combustion conditions, and are therefore more complex to evaluate than, for example, emissions of SO_2. However, there is a considerable amount of literature available on NO_x emissions, and estimation methods have developed across a number of years and, for road transport, have become considerably more sophisticated.

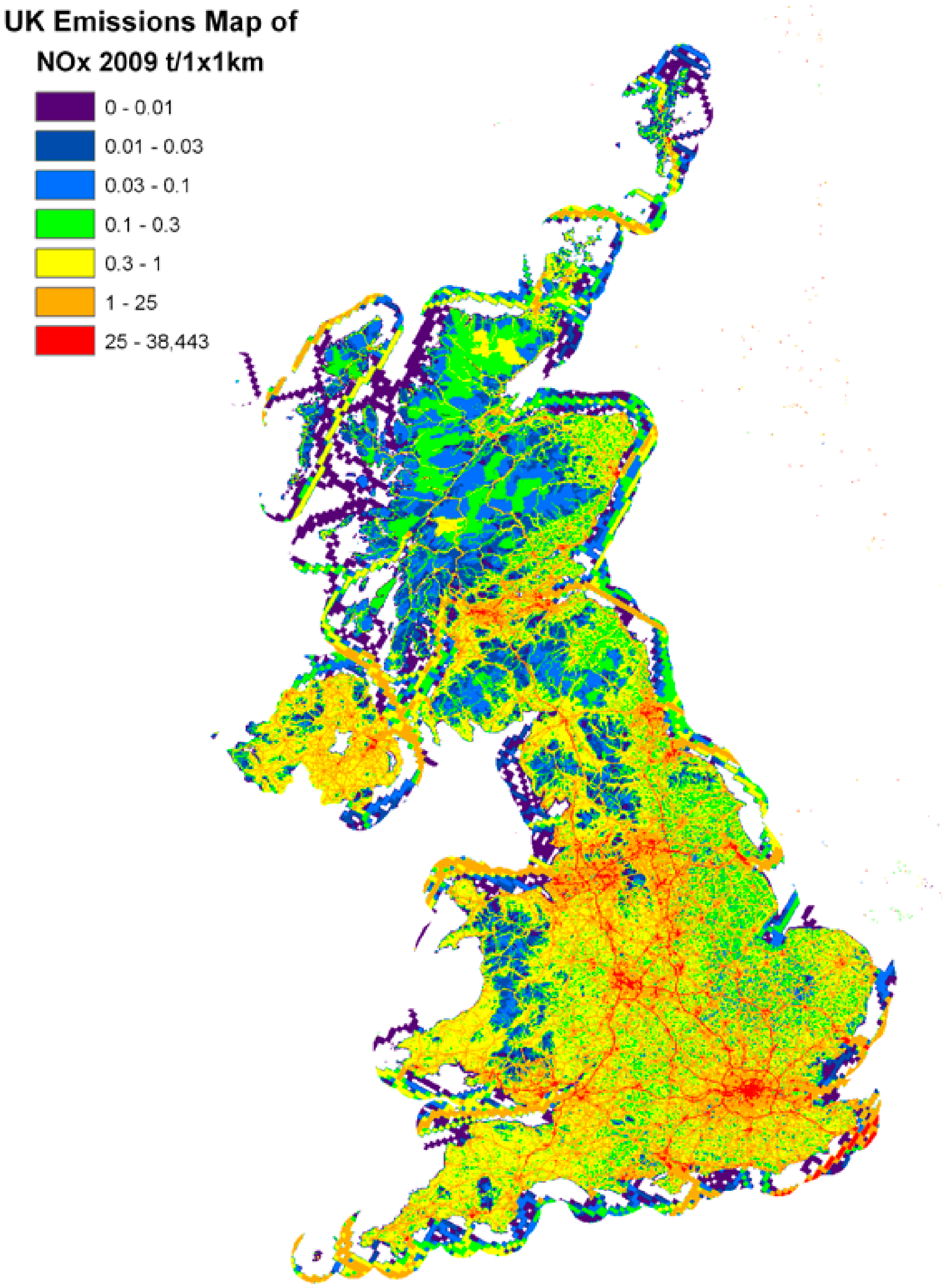

Figure 2.9: Mapped emissions of NO_x (expressed as tonnes NO_2 per km^2) (NAEI, 2011).

Emission estimates are available from a large number of individual industrial installations in the UK, and these are considered to be relatively accurate, as the emissions are not fugitive in nature and can therefore be measured by stack monitoring. The current levels of uncertainty in the national NO_x emissions total is given as a 95% confidence interval of ±8%, and has been determined by a Monte-Carlo analysis (Murrells *et al.*, 2010). It should be noted that this represents the uncertainty assigned to the absolute values of the national total. The uncertainties associated with historic trends with time are expected to be smaller. Nevertheless, verification studies in Section 2.3.2 show that real world inventory trends are likely to be significantly more uncertain than the estimated uncertainty levels from Monte-Carlo analyses.

Uncertainty estimates have also been made for projected emissions of NO_x and are ±14% for 2010 (Wagner *et al.*, 2009). The calculation requires expert judgement, thus increasing the overall uncertainty.

Uncertainties in spatial distribution

Emissions from road transport are the most important component in the majority of the grid cells. The distribution of these emissions is thought to be reasonably accurate, particularly on the major roads where traffic count data are available for individual road links. However, the NAEI does use national level assumptions on vehicle fleet profiles and speed profiles, etc. The increased incorporation of bottom-up information (such as that for London explained in Section 2.3.2) continues to provide improvements to the emission maps.

2.3.6 Climate change

Emissions of NO_x are reported as an 'indirect greenhouse gas' under international reporting requirements associated with climate change because NO_x is a tropospheric ozone precursor. The Royal Society has recently reviewed ground level ozone and includes the effect of climate change on ground level ozone (Royal Society, 2008). The Air Quality Expert Group has also reviewed the interaction between climate change and air quality in some detail (AQEG, 2007a).

It is expected that emissions of NO_x will be affected by national policies associated with the mitigation of greenhouse gas emissions (EEA, 2006). It is reasonable to presume that carbon dioxide emissions will decrease in future years; however, the impact on NO_x emissions will depend on how this decrease is achieved (AQEG, 2007a).

Carbon capture used in conjunction with coal-fired power stations is expected to give rise to increased emissions of NO_x per unit of energy generated, due to decreased plant efficiency (European Commission, 2007). However, total NO_x emissions from electricity generation would still be controlled under national and international legislation, and continued reductions in emission ceilings are expected (European Commission, 2008). The promotion of biomass as a fuel has the potential to significantly increase the emissions of air quality pollutants, in particular PM_{10} and NO_x. These kind of issues are being carefully considered at the national level. But as yet, there is no published national energy strategy which would give an indication of the extent to which biomass, nuclear, renewables or fossil fuels are expected to contribute to future national energy demands.

2.4 Ammonia (NH_3)

2.4.1 Overview

Air emissions of ammonia (NH_3) are dominated by the agricultural sector, and in particular manure management. Emissions from cattle dominate the UK total, accounting for 47% in 2008. Emissions from other livestock and synthetic fertiliser application accounted for 30% and 11% of the national UK total in 2007 respectively. As a result, the agricultural sector is responsible for 89% of UK NH_3 emissions in 2010 (CEIP, 2010; Defra, 2011).

NH_3 is primarily emitted from area sources and accurately measuring emissions, and introducing emission controls, is therefore generally more challenging than for combustion pollutants. As a result, the uncertainties associated with NH_3 emission estimates are larger than for combustion pollutants such as SO_2 and NO_x.

Emissions of NH_3 from livestock derive primarily from the degradation of urea (or uric acid for poultry) in excreta. NH_3 is emitted from the entire manure management process, during production, handling, storage and use or application to land. The N emission at each of these stages depends on a wide range of parameters, such as the amount of N in the feed, the levels of N excretion, whether the manure is stored dry or as a slurry, and whether application to land is by trailing shoe, injection or a range of other methods. Even the weather conditions during application can be an important determinand. Each of these variables will either impact on the levels of ammoniacal N or the extent to which the N in the manure will volatilise.

As a result, methods to estimate NH_3 emissions from livestock need to be suitably sophisticated to accurately reflect N emissions under different circumstances. In the UK, emissions are estimated from livestock sources using a mass-balance nitrogen-flow model (Webb and Misselbrook, 2004), which combines detailed partial emission factors (i.e. a specific emission factor for each category of livestock housing, manure storage, etc.) with statistics on activity data (livestock numbers, management practices, etc.). This approach is supported by an extensive programme of emissions measurement and provides the most reliable approach to estimate N emissions from manure management.

Emissions from agriculture also derive from urea- and ammonium-based inorganic fertilisers applied to crops and grassland. Emissions from fertilisers are estimated using an empirical model (Misselbrook *et al.*, 2004). The models, emission factors and activity data used to compile the inventory of ammonia emissions from UK agriculture are reviewed on an annual basis e.g. Misselbrook *et al.*, (2007).

Following the promotion of best practice in manure management and fertiliser use, NH_3 emissions have been decreasing substantially with time. For a number of years, emission projections have indicated that the UK will be very close to complying with the National Emission Ceilings Directive by 2010. Emissions reported for 2010 were 4% below the NECD target of 244 Gg-N (Defra, 2011).

2.4.2 NH_3 emission trends

Figure 2.10 shows NH_3 emissions in the UK (expressed as Gg-N).[5] Data on NH_3 emissions in the UK are reliable only from 1990 onwards; presenting incomplete emission estimates is not considered good practice, so estimates are presented for 1990 onwards only.

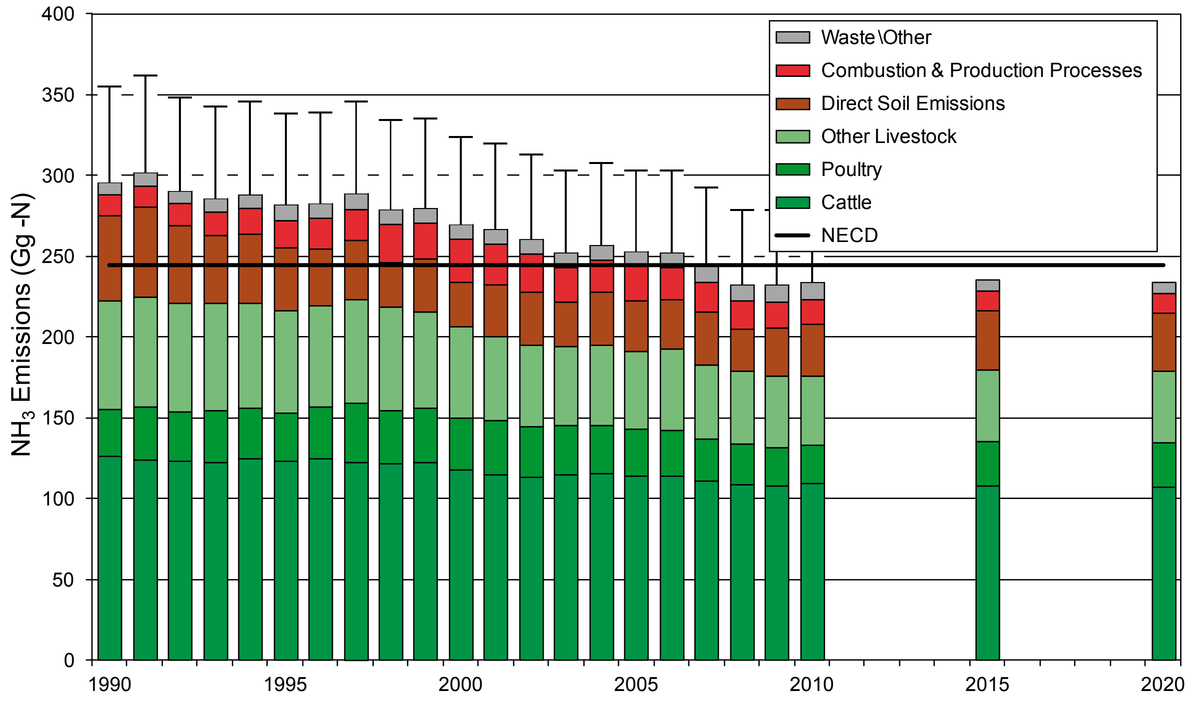

Figure 2.10: UK emissions of NH_3 (Gg-N) (Defra, 2011; EIONET 2012)[6].

Ammonia emissions from agriculture have declined from the peak values reached in the mid-1980s to early 1990s. These reductions are associated primarily with declining livestock numbers (in the period 1990-2007, total cattle numbers decreased by 15%, pigs by 55% and sheep by 31%) and fertiliser nitrogen use (43% decrease from 1990-2007) (Murrells *et al.*, 2010). A number of other factors have also contributed to the decline in emissions:

- Improved feed utilisation efficiency within the pig and poultry sectors has led to lower levels of N excretion.
- The laying hen sector has moved to housing types with improved manure management systems, which has resulted in lower ammonia emission factors.
- A small amount of uptake of mitigation methods across the industry has also been evident, such as low emission slurry spreading technology.

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[5] In the emission inventory field, it is usual to express emissions as a mass of NH_3. However, to ensure consistency with other chapters in this report, the emissions are quoted as mass of N (NH_3-N), and care should therefore be taken when comparing figures presented here with any other published emissions data.

[6] The projections used here are based on the UEP38 energy and 'business as usual' agriculture scenarios.

- Emissions from pig and poultry units are included in Integrated Pollution Prevention and Control (IPPC).

These reductions have been offset to some extent by two factors leading to increased emissions:

- Total poultry numbers in the UK have increased by approximately 22% over the period 1990-2007.
- There has been an increase in annual nitrogen excretion per dairy cow, associated with increasing milk production per cow.

While there has been a general downward trend in emissions from fertiliser applications to land, there is considerable year–to-year variability in this emission source. This largely reflects the year-to-year variability in the amount of urea and urea-based fertilisers used, as compared with ammonium-based fertiliser types (e.g. ammonium nitrate). Urea is associated with a much greater NH_3 emission than ammonium-based fertilisers, and small changes in the amount of urea used have a disproportionate effect on total emissions from fertiliser use. Variability in the proportion of urea fertilisers used is largely driven by price differentials.

Emissions from non-agricultural sources

The early generations of three-way catalysts used in road vehicles produced NH_3. This gave rise to NH_3 emissions from road transport through the 1990s. More modern three-way catalysts do not suffer from this problem to the same extent and NH_3 emissions from road traffic are now declining. The contribution to the total emission from road transport in 2008 is small at 4%. Other non-agricultural sources of NH_3 emissions include landfill, compost, sewage and combustion processes.

NH_3 emissions from natural sources

Emissions from natural sources (such as wild birds) are not included in reporting for the NECD and are not included in Figure 2.10. However, assessing the emissions from these sources is important for the modelling community and estimates are available (Dragosits and Sutton, 2008). Here, the term ‘natural’ is used to mean any source which is not covered by the NECD reporting guidelines. The NAEI includes three such sources – wild birds, wild animals, and human breath and sweat. These emissions amount to 7 Gg-N (Murrells *et al.*, 2010), although there are large uncertainties associated with the estimates. The sources do not vary much across the time series.

2.4.3 NH_3 emission projections and progress towards targets

As explained in both Sections 2.2 and 2.3, the UK is a signatory to the Gothenburg Protocol and the EU National Emission Ceilings Directive. Both include targets for NH_3 emissions of 297 Gg of NH_3 (244 Gg-N). The emission data show that the 2010 emissions were 4% below the NECD target (Defra, 2011).

Emission projections are available for selected years beyond 2010 out to 2050. But there is little decrease after 2010. These projections are based on ‘business as usual’ projections of livestock numbers and fertiliser use (Shepherd *et al.*, 2007) and continued trends in declining nitrogen excretion within the pig and poultry sector and increasing nitrogen excretion by dairy cows. Large pig and poultry farms come under IPPC legislation, so an increased uptake of mitigation methods is assumed within those sectors.

Projections of emissions from UK agriculture for 2020 under a 'no controls' scenario, a 'business as usual' scenario and a 'maximum feasible reduction' scenario give totals of 222, 202 and 175 kt NH_3-N respectively (Misselbrook *et al.*, 2009). The 'business as usual' scenario includes mitigation methods giving an emission reduction of approximately 10%.

Mitigation measures

A list of potential mitigation methods applicable to the agricultural sector are described in the Ammonia Mitigation Users Manual (Misselbrook *et al.*, 2008). Methods which are most readily applicable and would have a significant impact are those relating to manure applications to land. More costly measures relating to manure storage and livestock housing are associated with greater barriers to implementation and often less robust estimates of emission reduction efficiency. In the longer term, dietary manipulation to reduce nitrogen excretion (particularly in the cattle sector) combined with genetic improvement to increase efficiency of nitrogen utilisation may offer significant reduction potential.

2.4.4 Spatial distribution of NH_3 emissions

Figure 2.11 presents spatially disaggregated NH_3 emissions for the UK. The agricultural components of the emissions map are compiled using the AENEID model (Dragosits and Sutton, 2007; Hellsten *et al.*, 2008) which draws on local-level livestock data for the spatial distributions. There are high uncertainties associated with the livestock distributions, and as a result it is not considered appropriate to present the map at a 1 km x 1 km scale; 5 km x 5 km is used instead.

Under IPPC legislation, large pig and poultry units are required to report emissions to air. As a result, emissions data and location information from these installations can easily be captured. These sources are then mapped as point sources on the NH_3 map.

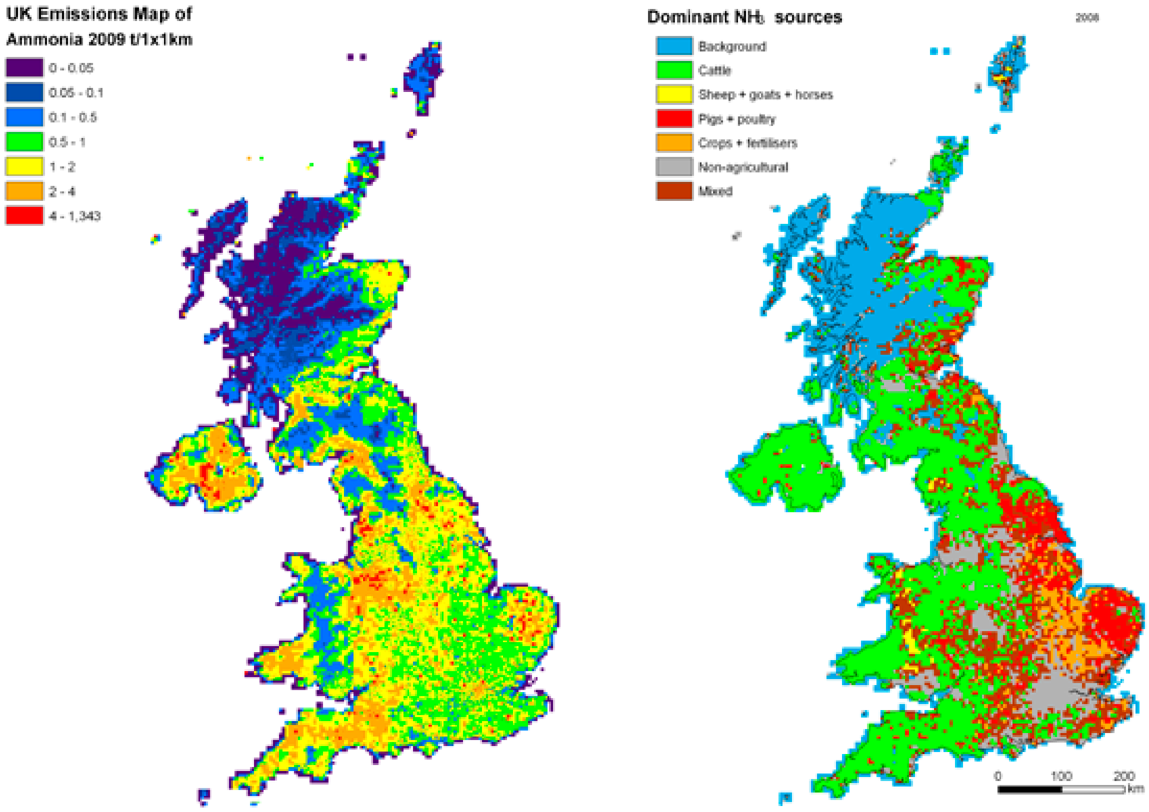

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Figure 2.11: Mapped emissions of NH_3 in 2009 expressed as kg per km^2 (NAEI, 2011) and the dominant sources of NH_3 emissions in the UK using 2008 data updated from Hellsten *et al* (2008).

High NH_3 emission densities are observed in the agricultural areas of the UK in Figure 2.11. For example, the high emissions in East Anglia are due to poultry and pig farming. Similarly high emission areas are evident in the south-west, the north of England and Northern Ireland, with emissions in these areas mainly due to cattle, pigs and poultry.

Non-agricultural emissions contribute relatively low levels of emissions. Road transport emissions are distributed to the road network, although as the relative contribution of this source is small compared to agricultural emissions, road transport emissions are not easily visible on the 5 km x 5 km emissions map. Other industrial sources are mapped as point sources and are therefore also not easy to see.

2.4.5 Uncertainties in NH_3 emissions

In the past, modelling studies suggested that the emissions inventory was not capturing all the NH_3 sources in the UK. Over the last several years a number of additional sources have been identified, quantified and included in the emissions inventory. This provides a more rigorous emissions inventory, although it may be that the UK now includes a number of sources which are not commonly reported in NH_3 emission estimates from other European countries.

Uncertainties associated with the NH_3 emissions total are relatively high compared with other pollutants. Emissions from the agricultural sector are affected by a large number of factors which make the interpretation of experimental data difficult and emission estimates uncertain (DOE, 1994). Emission estimates for non-agricultural sources such as wild animals are also highly uncertain. Unlike other pollutants, for example NO_x, a few sources dominate the inventory and there is therefore limited potential for error compensation. As a result, any bias in the emission estimates from these large sources will give rise to a relatively large error in the emission total.

An analysis of uncertainties in the agriculture emissions inventory was conducted by Webb and Misselbrook (2004) using a Monte-Carlo analysis. This gave a 95% confidence interval for the total inventory estimate of ±20%. However, this approach cannot account for unidentified sources of error and bias. While recent research has improved the robustness of many emission factors used within the inventory, knowledge gaps still remain. This is particularly true for:

- Free-range pig production systems.
- Free-range poultry production systems.
- A number of potential mitigation methods.
- A number of farm management practices.

The uncertainty associated with the trend in total emissions has not been evaluated, but it is expected to be considerably smaller than the ±20% uncertainty assigned to absolute emissions. This is because year-to-year changes are reasonably well assessed by capturing changes in animal numbers.

Uncertainty estimates have also been made for projected emissions of NH_3, and are ±17% for 2010, increasing slightly for 2015 and 2020 (Wagner *et al.*, 2009). The calculation requires expert judgement, thus increasing the overall uncertainty in emissions.

2.4.6 Climate change

NH_3 emission projections to 2050 are available, although these are highly uncertain, and so only speculative observations may be made about the impacts of climate change on emissions.

Livestock numbers and fertiliser projections beyond 5-10 years are extremely uncertain because of the large number of national, European and global variables influencing sectoral activities, so projections for 2025 have been carried forward to 2050 with no changes, except for dairy cow numbers where continued improvements in productivity are likely to result in a decline in numbers for a given total milk output.

Predicted temperature increases using the UKCIP02 scenario have been included in the emission projections for fertiliser applications, leading to a small increase from that source. In practice, adaptations to climate change within the agricultural sector in terms of management practices are likely to have a greater effect on ammonia emissions than the purely physical effects of a temperature increase.

Hotter, drier summers may lead to cattle being housed, rather than grazed at pasture, for a greater proportion of the year, most likely resulting in increased ammonia emissions per animal. Wetter spring weather may result in a greater proportion of livestock manure being applied to land under hotter summer conditions, again likely to result in increased emissions. Any emission reductions due to further declines in livestock numbers, improved efficiency and uptake of mitigation methods are likely to be offset therefore by increases due to changing management practices and increasing temperatures. Most of the known effects of climate change are therefore likely to increase ammonia emissions, all other factors remaining constant, but the magnitude of the change is not known.

Cost–benefit studies have recently been undertaken to assess the most effective way of reducing greenhouse gas emissions from the agricultural sector in the UK, and importantly these studies have also included NH_3 (Anthony *et al.*, 2009). The UK Government is currently considering options for future agricultural policies relating to climate change, which will therefore also determine the impact on NH_3 emissions. In doing this, the Government is working closely with the farming community to provide guidance on best practice.

The interaction between climate change and NH_3 emissions has also been reviewed by AQEG (2007a).

2.5 Non-methane volatile organic compounds (NMVOCs)

2.5.1 Overview

Emissions of non-methane volatile organic compounds (NMVOCs) arise from a wide range of sources; they are produced by combustion, and emitted from solvent and product use/manufacture, and from the extraction and distribution of fossil fuels. In 2008 combustion sources contributed 25% to the UK emissions total, with solvent use contributing 42%, and the extraction and distribution of fossil fuels 20% (CEIP, 2010).

NMVOC emissions from combustion are dominated by emissions from road transport and are dependent on a wide range of parameters. NMVOCs are released as both exhaust and evaporative emissions.

Emissions of NMVOCs during product and solvent use can be estimated using a mass-balance approach because the solvent in the product is usually completely released to air. This is not the case for emissions associated with product manufacture, because the emissions are often fugitive in nature and therefore difficult to estimate. This latter point is also the case for many of the different sources associated with fossil fuel extraction and distribution.

NMVOCs are a group of compounds and are usually expressed as a total mass emission. However, it is possible to speciate the emissions into individual components for input into, for example, ozone models.

Since their peak in 1990, NMVOC emissions from all major source groups have declined. The latest emissions figures confirmed that the UK met the National Emissions Ceilings Directive (NECD) 2010 target. Emissions of NMVOCs reported for 2010 were 34% below the NECD target value of 1200 Gg.

2.5.2 NMVOC emission trends

Figure 2.12 shows the UK emissions for NMVOCs from 1970 to 2008, along with projected emission estimates to 2020.

Stationary combustion

Historically, emissions from stationary combustion sources were dominated by coal combustion in the domestic sector. However, as coal has increasingly been replaced by other fuels, emissions have fallen with time, and a wide range of smaller sources now contribute to the emissions from stationary combustion – electricity generation now comprising only 5% of stationary combustion sources.

Road transport

Emissions of NMVOCs from the road transport sector increased steadily until the early 1990s, reflecting increased activity levels. Emissions of NMVOCs from road transport have been declining since the early 1990s due to the introduction of three-way catalysts and the fitting of carbon canisters to control evaporative emissions from petrol cars. In addition, the vapour pressure of petrol fuel sold during the summer months has been reduced as a consequence of EU fuel quality directives. As a result emissions from this sector have continued to fall with time.

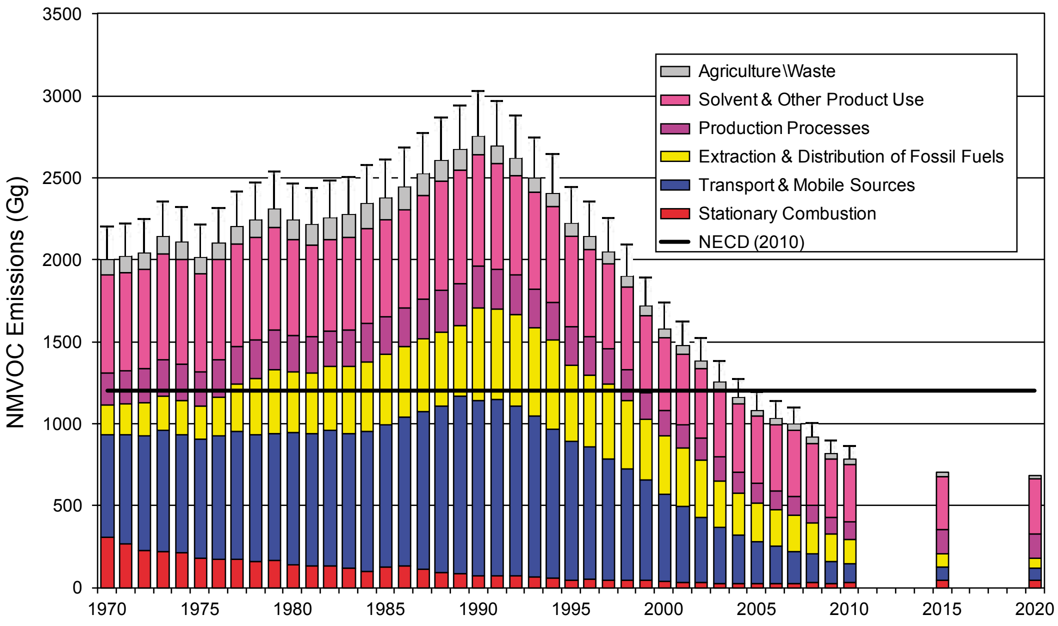

Figure 2.12: UK emissions of NMVOCs (Gg) (Defra, 2011; EIONET 2012)[7].

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[7] The projections used here are based on the UEP38 energy scenario.

Extraction and distribution of fossil fuels

The larger emissions in this sector are from refineries and the activities associated with the distribution of petrol (emissions from refineries and storage depots, storage at petrol stations and refuelling). Legislation has been introduced to reduce emissions from these sources. General improvements in operating practices have also been implemented, giving rise to reductions in NMVOC emissions.

Offshore oil and gas activities and leakage from gas mains are also included in this sector. Improved offshore operating practices and mains pipeline replacement have given rise to the gradual reduction in emissions from these sources.

Solvent and other product use

This source sector includes the use of paints, inks, degreasers, etc., and other products. The use of paints and similar products has been increasing with time. However the amount of solvent used in paints has decreased. This has been possible through improvements to the products, but has primarily been driven by legislation. For example, the Solvent Emissions Directive, which passed into UK law in 2002, required operators using large quantities of solvents to present solvent management plans showing effective management practices. The car paint spraying industry provides an example of how practices have changed. In the past, the car industry used paint with a high solvent content. As paint technology improved, it was possible to greatly reduce the solvent content without affecting the quality of the finish. In addition to this, the spraying process was also improved, reducing solvent losses and allowing solvent recovery for reuse.

NMVOC emissions from vegetation

Trees and a range of other higher plants emit volatile organic compounds. The levels of emission are highly species dependent, and vary either with temperature or temperature and sunlight. As these emissions are classified as 'natural' they are not included in official UK emission totals but are reported for information. The current estimate for the UK is 91 Gg of NMVOC for 2008. The current methodology in the NAEI uses a single value for emissions from forests for all years, and does not take into account the variation in temperature and incident sunlight from year to year. More information can be found in the Royal Society report on ozone (Royal Society, 2008).

2.5.3 NMVOC speciation

NMVOCs are a group of compounds and, whilst it is usual to express them as a total mass, there are occasions when identifying the individual compounds is important. This is primarily for use in atmospheric chemistry models associated with tropospheric ozone formation. A table of the top 50 compounds can be found in Murrells *et al.* (2010). This source also includes a table of emissions weighted by POCP (photochemical ozone creation potential), which ranks the emissions in terms of their importance in ozone formation. Whether ranked by mass of emission or POCP-weighted emission, the top three compounds emitted are ethanol, butane and ethane. Details of the methodology for speciating NMVOC emissions in the UK can be found in Passant (2002) .

2.5.4 NMVOC road transport emissions verification

An important issue for NMVOC emission estimates is the degree to which they reflect real world behaviour. Hourly observations of over 25 VOC species have been made at a kerbside location, Marylebone Road, in central London since 1997. Over the period 1997-2008, almost all VOC species showed marked downwards trends in their 90-day rolling mean concentrations. These trends represent a decrease in concentration of between 10% and 20% per year. Figure 2.13 shows the observed trend in the cumulative 90-day rolling mean concentrations for the 16 most important C_2-C_8 VOC species by mass (excluding ethane) over the 1997-2008 period. This has been over-plotted with the NAEI UK road transport VOC emissions for the same period.

The agreement in shape between the time records of the observed total VOC concentrations and the road transport emissions is striking and shows that the assumptions made concerning the uptake and performance of three-way catalysts and carbon canisters for evaporative emission control clearly reflect real world behaviour.

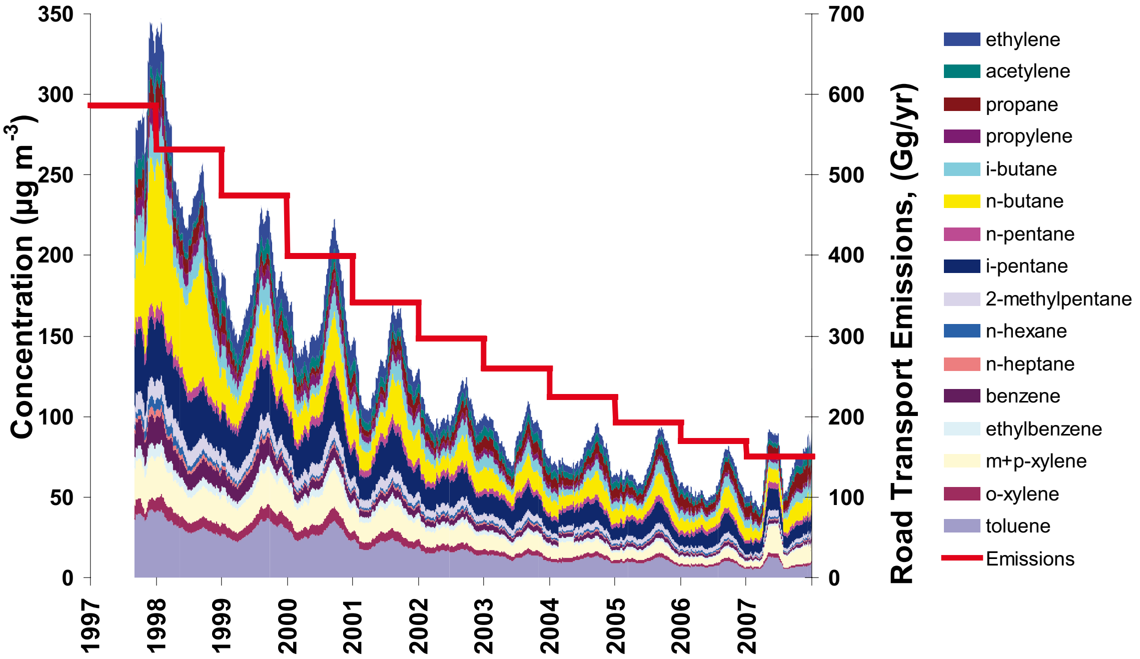


Figure 2.13: 90-Day rolling mean NMVOC concentrations (Marylebone Road) compared with NAEI road transport emission estimates (2008 concentration data are provisional). Derived from ratified AURN data (http://www.airquality.co.uk) and NAEI emissions data (Murrells et al., 2010).

2.5.5 NMVOC emission projections and progress towards targets

As explained in both Sections 2.2 and 2.3, the UK is a signatory to the Gothenburg Protocol and is bound by the EU National Emission Ceilings Directive. Both include 2010 targets for NMVOC emissions of 1200 Gg.

The emissions reduction provided by three-way catalytic convertors and carbon canisters for evaporative emissions control in the road transport fleet has been such that the UK has always appeared to be on target to achieve the NECD ceiling for NMVOCs. In fact, emissions have been lower than the 2010 ceiling for several years.

After 2010, projections show little reduction in emissions. This is primarily because it is difficult to estimate the future levels of production and use of substances containing NMVOCs, for example paint. As a result, emission projections for many of the sources are assumed to be constant with time.

New ceilings for 2020 are expected to be proposed as part of the revision to the Gothenburg Protocol and the NECD. So it will be important that NMVOC projections are robust enough to support the UK Government in its negotiations, and in determining whether any proposed projections are realistic.

2.5.6 Spatial distribution of NMVOC emissions

The NMVOC emissions map for the UK is shown in Figure 2.14. A large proportion of emissions are caused either as a result of the activities of people in and around their homes (e.g. domestic solvent use or domestic combustion), or by widespread industrial activities such as small-scale industrial coating processes, dry cleaning shops, and small bakeries, which are present in towns and cities throughout the UK. Consequently the resulting emissions map is highly correlated with population density.

The NMVOC map includes a large number of point sources, such as oil refineries, crude oil terminals, large combustion plant, sites of chemicals manufacture and iron and steel processing, and factories in the food and drink sector. Unlike the map presented previously for NO_x (Section 2.3.4), the NMVOC map has little major road definition except where the major roads go through rural areas. This reflects the fact that petrol cars, the dominant source of NMVOC emissions, contribute a larger portion of road transport emissions in urban areas and a lower portion of emissions on motorways and major roads.

2.5.7 Uncertainties in NMVOC emissions

Uncertainties in the NMVOC emissions inventory have been assessed using a Monte-Carlo approach, giving a 95% confidence interval for the emissions estimate of -9% to +10% (Murrells *et al.*, 2010).

This level of uncertainty is higher than that for NO_x and SO_2 emissions. This is due in part to the difficulty in obtaining reliable emission factors or emission estimates for some sectors (e.g. fugitive sources of NMVOC emissions from industrial processes and natural sources) and partly due to the absence of good activity data for some sources. The NMVOC emissions inventory does contain more individual sources than that for any of the other pollutants in the NAEI. As a result, there is a high potential for error compensation, and this is responsible for the relatively low levels of uncertainty presented here.

Uncertainty estimates have also been made for projected emissions of NMVOC, and are ±10% for 2010 (Wagner *et al.*, 2009). The calculation requires expert judgement, and the results are therefore themselves uncertain.

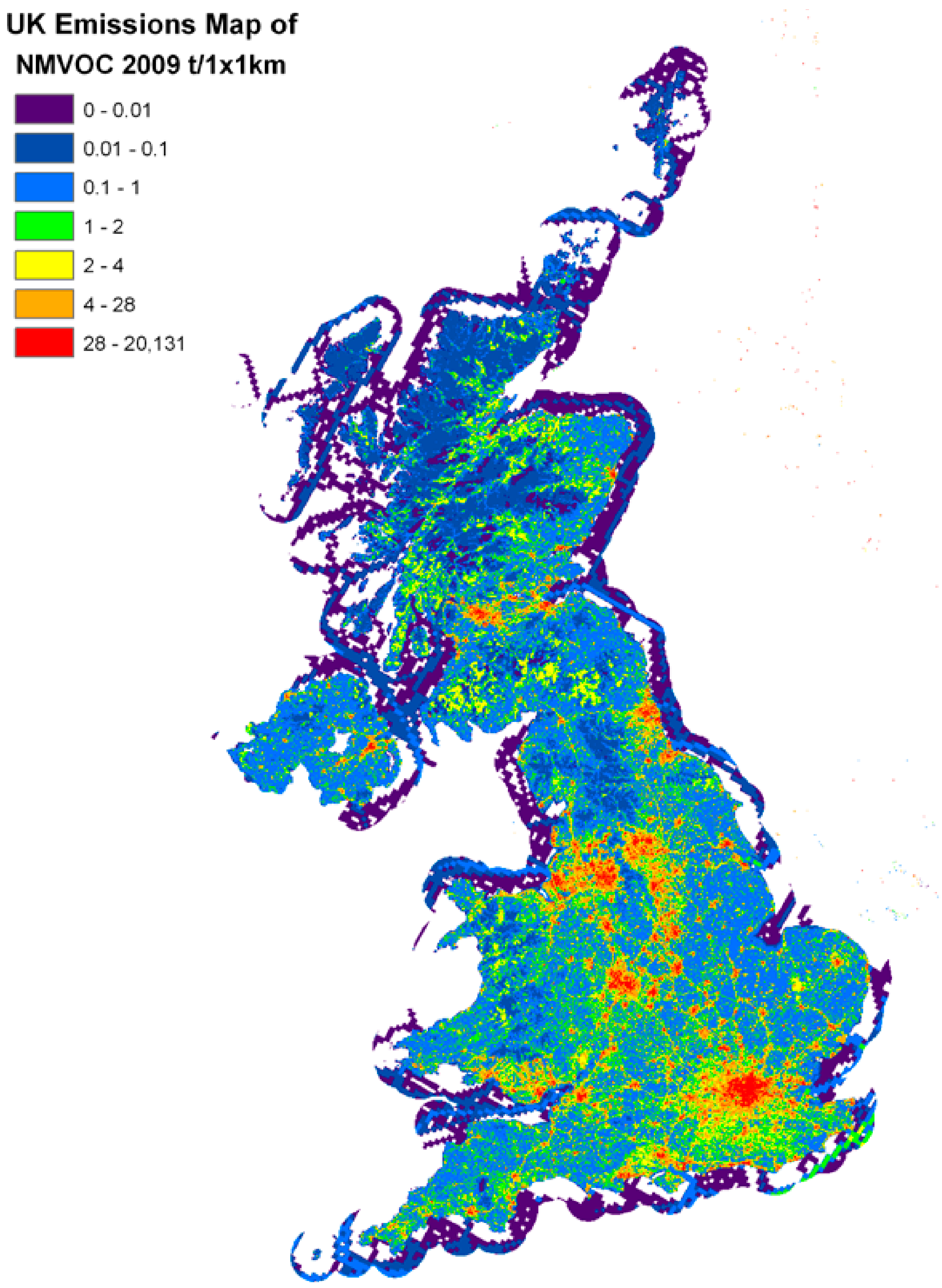


Figure 2.14: NMVOC emissions map (expressed as tonnes per km²) (NAEI, 2010).

2.5.8 Climate change

NMVOC emissions are reported as an 'indirect greenhouse gas' under international reporting requirements associated with climate change because they are tropospheric ozone precursors.

Climate change is expected to have a significant effect on NMVOC emissions from vegetation. Given that the vast majority of forested areas in the UK are managed, it is possible that there will be a gradual shift to species which are better suited to warmer climates. Whilst emissions of NMVOCs do vary considerably between closely related tree species, it is also true that species found in the Mediterranean regions tend to be higher emitters of NMVOCs. So it is possible that there will be change which gives rise to higher emissions of NMVOCs. A more detailed assessment may be found in AQEG (2007a).

NMVOC emissions from combustion sources are expected to decrease as the drive to reduce greenhouse gas emissions continues (EEA, 2006). This will depend on the extent to which fossil fuel consumption is reduced, either through energy efficiency measures or the increased use of biomass and biofuel. Emissions from solvent use and other processes will be driven by tighter legislation, but this is not expected to be linked to climate change (European Commission, 2008).

Chapter 3 Concentrations and Deposition of Sulphur, Nitrogen, Base Cations and Ozone in the UK

Summary

- Monitored concentrations of sulphur dioxide (SO_2) over rural UK declined from an average of 12 ppb in 1988 to 0.5 ppb in 2008, while for nitrogen dioxide (NO_2) the concentration declined from 6 ppb in 1987 to 3 ppb in 2008.
- Concentrations of ammonia (NH_3) averaged over rural UK have changed little over the last decade. However, there have been reductions in areas in which emissions from pig and poultry production dominate the sources, while in remote regions and some areas in which cattle and sheep dominate the sources, there have been small increases.
- Concentrations of acidity, non-marine sulphate (SO_4^{2-}) and non-marine chloride (Cl^-) in precipitation have declined by 85%, 75% and 95% respectively over the period 1986 to 2008. The trend in deposited acidity is dominated by changes in non-marine SO_4^{2-} which accounts for 75% of the trend.
- Annual dry deposition of SO_2 to the UK declined by 93% between 1986 and 2008 whereas wet deposition declined by 57%, leading to the largest reductions in sulphur deposition in the Midlands and east of the UK and the smallest in the uplands of the north and west.
- The total deposition of nitrogen (which is fairly evenly split between the oxidised and reduced forms) has changed little (-13%) between 1988 and 2008 from 389 kt yr-1 to 336 kt yr-1, despite large (58%) reductions in emissions of NO_x and 21% reductions in emissions of NH_3.
- Spatial distributions of sulphur and nitrogen deposition arising from UK emissions have changed over the last 20 years, with greatly reduced exports of both sulphur and nitrogen and a larger fraction of UK emissions being deposited within the UK. These changes were caused by increases in the atmospheric processing (oxidation) and deposition of sulphur and nitrogen compounds. The cause of these observed non-linearities in the relationship between emissions and deposition are quite well understood for sulphur compounds, but in the case of oxidised nitrogen, while they imply a steady increase in rates of oxidation of NO_x to NO_y with time, the mechanistic detail remains unknown.
- The main consequence of the ~58% reduction in UK emissions of oxidised nitrogen is that exports from the UK have declined by nearly 50% while deposition within the UK has changed by only 23%.
- Peak ozone (O_3) concentrations in rural areas of the UK declined by about 30% between 1986 and 2007, while the hemispheric background has increased by roughly 0.2 ppb annually (~4 ppb over the same period). In addition, the seasonality of ozone exposure has changed with increases in spring concentrations in excess of 40 ppb. The changing climatology of ozone is particularly important for ozone sensitive vegetation as discussed in Chapter 5. Hot, dry summers, such as 2003, still lead to peak concentrations in excess

of 100 ppb, which are a threat to human health and vegetation.

- Changes in climate are likely to influence the atmospheric processing and deposition of pollutants. In the case of ground level ozone, the effects of anticipated changes in climate between 2000 and 2050 are likely to erode some of the benefits of control measures on ozone precursor emissions over Europe.

3.1 Introduction

The objective of this chapter is to present the concentration and deposition fields for the pollutants concerned with acidification, eutrophication and ozone in the UK and to show how these have changed since the time of maximum emissions in the 1950s, or from the point when the networks monitoring air and rainfall composition were established in 1986, or later for ammonia (NH_3), nitric acid (HNO_3) and aerosols. There are a large number of maps and country-scale budgets for the individual components of acid deposition and eutrophication, including concentration fields for each of the chemical species involved (sulphur dioxide (SO_2), sulphate (SO_4^{2-}), nitric oxide (NO), nitrogen dioxide (NO_2), nitric acid (HNO_3), nitrate (NO_3^-), ammonia (NH_3), ammonium (NH_4^+), and sodium, chloride, magnesium and calcium ions), deposition fields for the wet and dry deposition of each component and totals for oxidised nitrogen, reduced nitrogen, total sulphur, anthropogenic sulphur and sea-salt sulphur. To present a concise account of the current position in the UK and the trends over the last 20 years within this chapter, only the principal charts and maps are presented here. The full set of maps and budget values may be accessed at http://www.uk-pollutantdeposition.ceh.ac.uk/image/tid/7.

3.2 Acidity in precipitation

The original interest in sulphur and nitrogen deposition was generated by observations of a gradual acidification of precipitation throughout northern Europe between the mid-1950s and late 1960s (Odén, 1968). Over this period precipitation pH values lower than pH 4.3 were observed in most countries bordering the southern North Sea (Sweden, 1971) extending south into large areas of central Europe. In the UK the pattern of acidification showed a strong gradient between west and east coasts with the smallest annual mean acidity in north-west Scotland and a gradual increase in acidity and concentrations of SO_4^{2-}, NO_3^- and NH_4^+ towards the east coast (Fowler *et al.*, 1982). These early measurements of rainfall composition in the UK did not provide complete coverage of the country and it was not until 1986 that networks with full coverage of the UK were in place. The acidity of precipitation in the UK in 1986 showed annual mean values ranging from 90 $\mu eq\ H^+\ l^{-1}$ in the East Midlands to 10 $\mu eq\ H^+\ l^{-1}$ in northern Scotland (Figure 3.1a). The annual mean conceals much of the variability between events, and individual rainfall events showed acidities as high as pH 3.0 (1000 $\mu eq\ H^+\ l^{-1}$) in an annual rainfall weighted mean of pH 4.2 (Fowler *et al.*, 1982). By 2008 rainfall acidity had declined everywhere in the UK (Figure 3.1b). The maximum values for the annual weighted mean acidity had declined from 90 $\mu eq\ H^+\ l^{-1}$ in 1986 to 20 $\mu eq\ H^+\ l^{-1}$ in 2008. The trend with time across all sites is shown in Figure 3.2, with all site years of data included in the analysis. The annual mean rainfall acidity

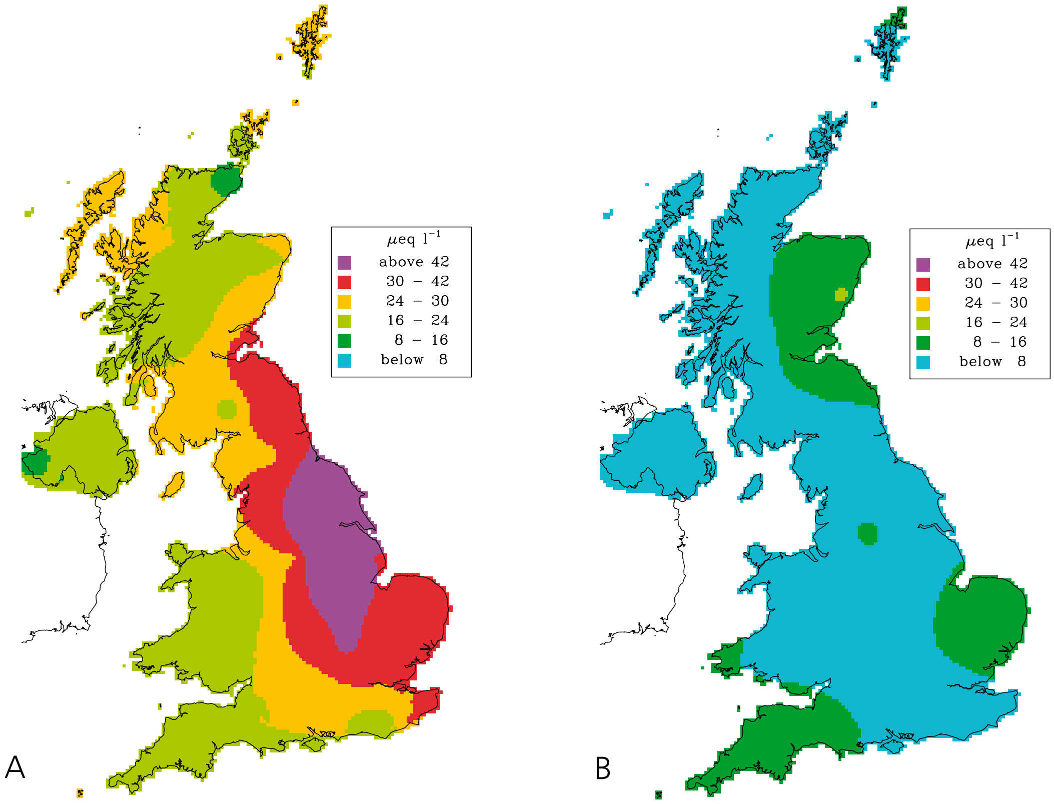


Figure 3.1: The spatial distribution of precipitation acidity (μeq H^+ l^{-1}) in (a) 1986 and (b) 2008 . Figure compiled using data from UKEAP (2010).

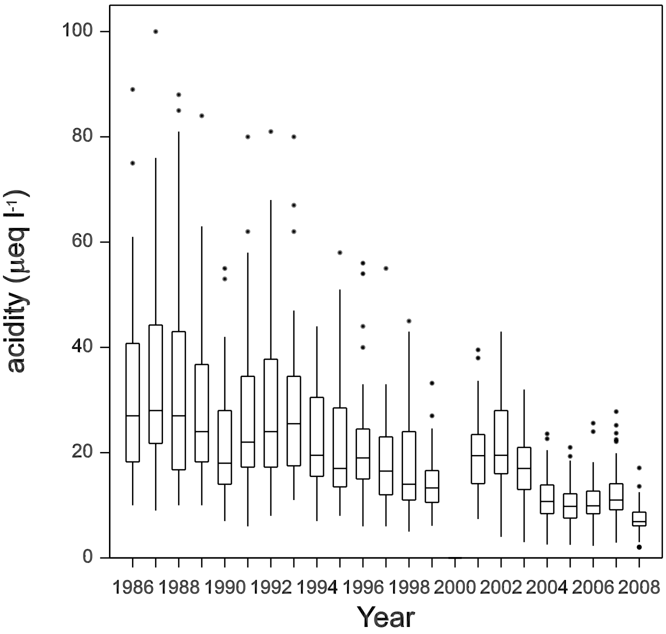


Figure 3.2: The trend in rainfall-weighted mean annual acidity at all sites in the UK monitoring network between 1986 to 2006 (Regression analysis showed that acidity = 33.7 - 1.11 * (no. of years since 1986) P=0.000.) Figure compiled using data from UKEAP (2010).

over the UK declines from 32 µeq H$^+$ l^{-1} in 1986 to 7 µeq H$^+$ l^{-1} in 2008 and it is notable that the range in the mean annual acidity across the country declines from 80 µeq H$^+$ l^{-1} to 15 µeq H$^+$ l^{-1} over the 20 years. The change in rainfall acidity over the last two decades has been dramatic, rainfall in the UK has lost the high acidities common prior to 1995. The absolute values for acidity are very small and the range over the country is also small. A feature in recent maps of rainfall acidity is the area of high acidity in the south-west approaches to the UK which appear to be due to emissions of sulphur from shipping which make a substantial contribution to both sulphur and acidity in rainfall in these coastal areas.

By 2008, not only has the mean acidity declined to values close to background levels found in remote areas, but there are no sites in the network with average values greater than 20 µeq H$^+$ l^{-1}. Trends in rainfall acidity at individual sites all show statistically significant declines over the monitoring period and the acidity in the most polluted region (eastern England) is now close to that in the cleanest parts of the country in 1986. This large trend with time is due primarily to the reduction in sulphur emissions.

3.3 Sulphur

The changes in emissions outlined in Chapter 2 are large; in the case of sulphur, the peak emission in 1970 was approximately 3.2 Tg SO_2-S which declined by 2008 to 0.256 Tg SO_2-S, representing a reduction of approximately 90% in sulphur emissions. A

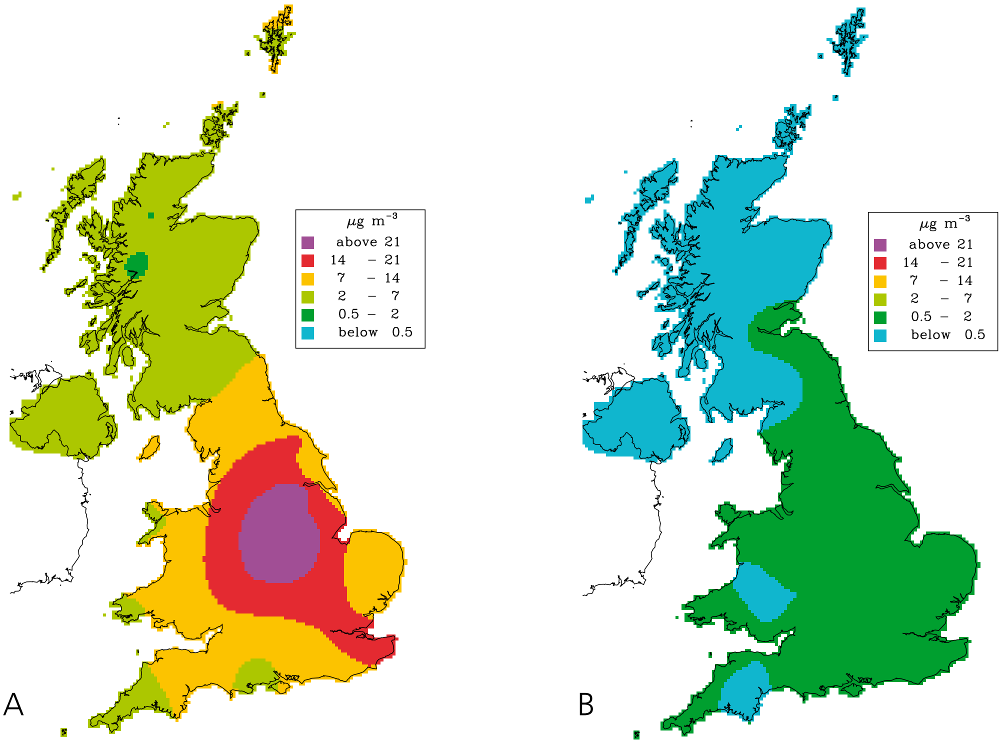


Figure 3.3: Annual average SO_2 concentrations (µg m-^{3}) across the UK in (a) 1987 and (b) 2008. Figure compiled using data from UKEAP (2010).

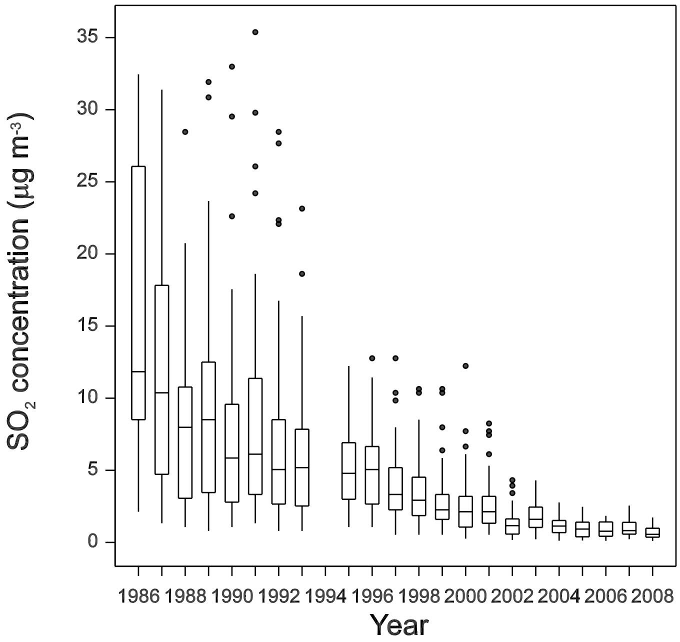


Figure 3.4: The trend in rural SO_2 annual mean concentration measurements in the UK between 1986 and 2008 (Data for 1994 were excluded for Quality Assurance reasons.) Figure compiled using data from UKEAP (2010).

substantial fraction of the decline in emissions occurred before the monitoring network was fully established in 1986 (Figure 2.1), but the magnitude of the reduction during the monitored period remains large and presents an opportunity to show the effects of the large changes in emissions on concentrations and deposition fields and the overall budget of sulphur in the atmosphere over the UK.

The concentrations of SO_2 in 2008 are largest in the urban and suburban areas of the country, with values of a few ppb, and in the rural Midlands and home counties, with concentrations of 1 to 2 ppb (Figure 3.3b). Elsewhere, in rural areas and especially in the west and north of the UK, SO_2 concentrations are low at below 0.5 ppb (<1.3 µg SO_2 m^{-3}). The spatial pattern of concentrations of SO_2 in its broadest sense is similar to those in the period of high emissions, with the highest values in the Midlands, and with a west to east gradient with the lowest values along the west coast. The magnitude of the reduction in SO_2 concentrations is remarkable, with values in the Midlands of typically 0.5 ppb in 2008 compared to values in the 1970s of 30 ppb (Fowler *et al.*, 1982). Concentrations of SO_2 averaged across the network stations decreased from 18 ppb (51 µg m^{-3}) in 1986 to 0.5 ppb (1.5 µg m^{-3}) in 2008, showing a halving every 3 to 4 years (Figure 3.4).

3.3.1 Aerosol SO_4^{2-} concentrations

Emissions of SO_2 disperse and undergo chemical transformation in the atmosphere to SO_4^{2-} both in the gas phase and in cloud and rain droplets (Holloway and Wayne, 2010). The SO_4^{2-} produced is in particulate form and is generally associated with NH_4^+ and

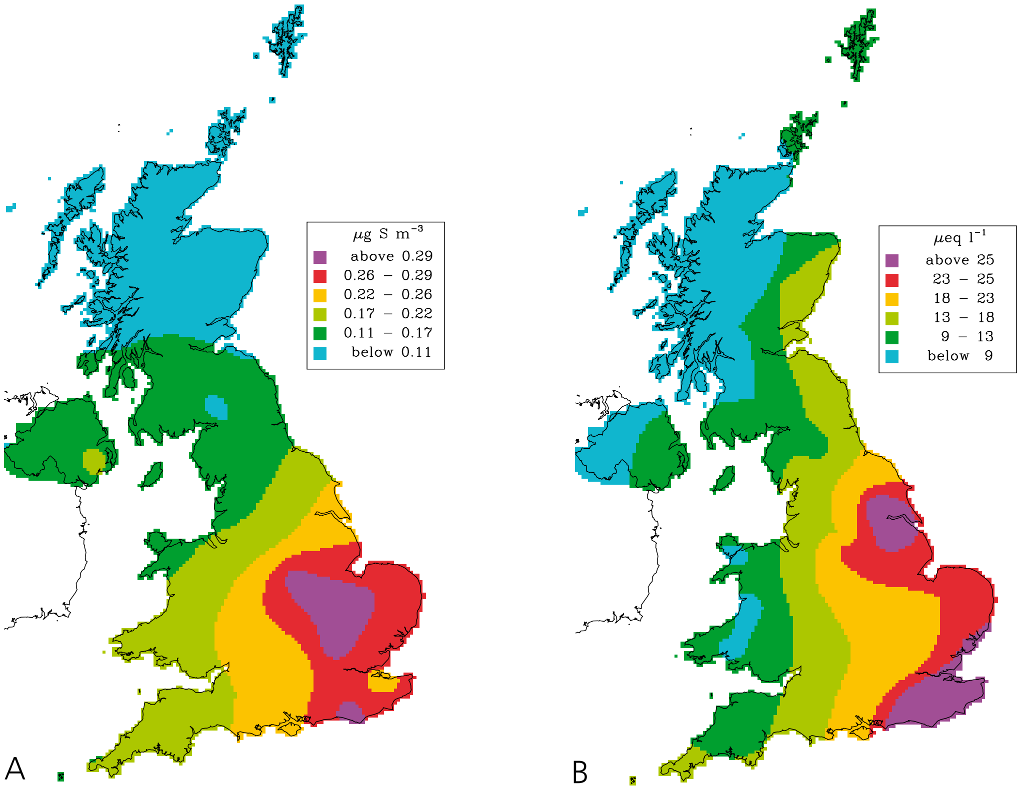


Figure 3.5: (a) Measured aerosol SO_4^{2-} concentrations in the UK 2008, (b) Rainfall-weighted non-sea-salt SO_4^{2-} concentrations in the UK for 2008. Figure compiled using data from UKEAP (2010).

NO_3^-. Aerosol SO_4^{2-} has been measured at sufficient UK sites to provide a countrywide map over the last decade; the first such maps were presented in NEGTAP (2001). The concentrations of aerosol SO_4^{2-}, present largely in the sub-micron fraction, show a smooth gradient from the lowest values in north-west Scotland at 0.2 μg m^{-3} to the largest values in south-east England at 0.6 μg m^{-3}. The gradient in aerosol concentration between the west and east coasts is similar in magnitude to the gradient in SO_4^{2-} in rain presented in Figure 3.5(b), because precipitation scavenging is the main removal pathway for aerosol SO_4^{2-} (Fowler, 1980). Within the 10-year dataset of measured aerosol concentrations in the UK there are no clear trends.

3.3.2 Deposition of sulphur in the UK

The removal of sulphur compounds from the atmosphere occurs through dry deposition of gaseous SO_2 and aerosol SO_4^{2-} to terrestrial and marine surfaces and wet deposition of SO_4^{2-} and the turbulent deposition of cloud-water droplets, the latter sometimes being known as occult deposition (Fowler *et al.*, 1991).

3.3.3 Wet deposition

Total wet deposition is calculated by combining the measured concentrations of SO_4^{2-} in precipitation with annual precipitation. The precipitation chemistry network

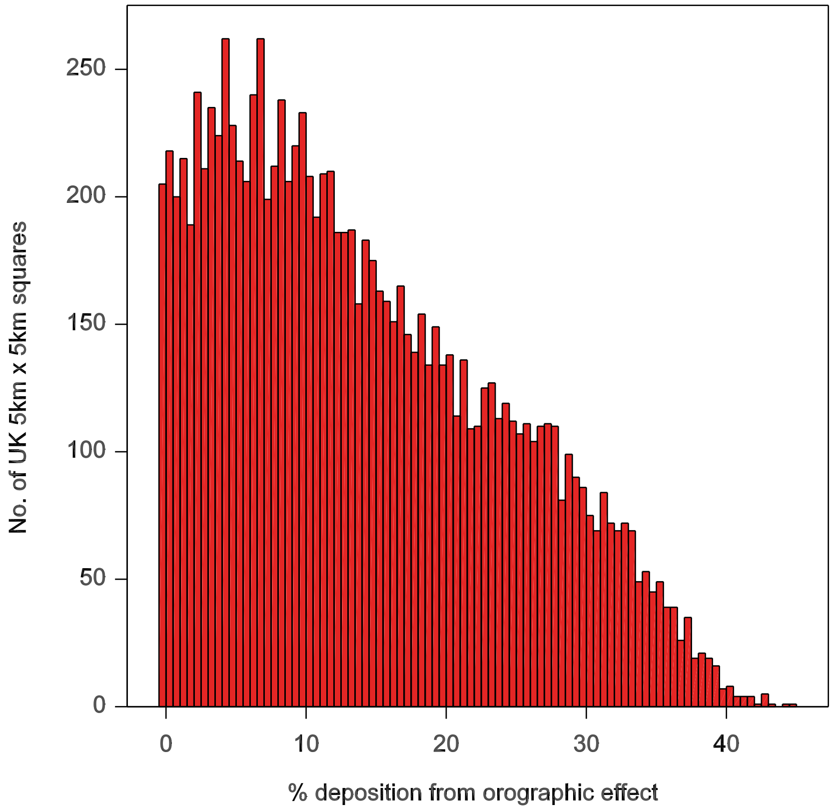


Figure 3.6: The orographic component of wet deposition expressed as a percentage of the total deposition within each grid square. Figure derived from CEH measurements of sulphate in 2008.

is restricted to just 38 rural sites distributed throughout the UK and mainly located on low ground. Measurement of wet deposition at high elevation sites is particularly difficult as a consequence of snow and wind, and the need to locate the collecting funnel at heights typically 2 m above ground level to reduce contamination from sources on the ground; this leads to substantial underestimates of precipitation at windy and high altitude sites.

Table 3.1: Additional deposition of sulphur and nitrogen compounds through the orographic enhancement of wet deposition over the UK uplands. Table derived from CEH measurements of sulphate in 2008.

Component	Rain* rain ion concentration	Orographic addition	UK wet deposition	% Wet deposition from orographic effect
Oxidised sulphur	84.8	17.1	81.1	21.0%
Oxidised nitrogen	84.4	16.6	80.7	20.6%
Reduced nitrogen	116.5	23.3	111.5	20.9%

These limitations prevent the direct measurement of wet deposition at high elevation sites where the largest precipitation, and therefore where a substantial fraction of the wet deposition, occurs. It is necessary to quantify the wet deposition over the high elevation and high precipitation areas of the country to avoid bias in the mapping of wet deposition which underpins a substantial part of the analysis of potential effects of the deposition. There is a further complication due to the mechanisms which generate the higher precipitation in the uplands of the UK. The mechanism is known as seeder-feeder scavenging and refers to the washout of hill cloud droplets by rain falling through hill clouds which envelop the uplands in wet weather. Hill cloud incorporates much of the aerosol burden in the boundary layer air advected up the hill slope, and some of the primary SO_2 as described by Choularton et al. (1988). This causes the concentration of major ions in rain to increase with altitude along with the rainfall amount, resulting in large increases in wet deposition with altitude as shown in field experiments in the UK uplands in Cumbria and Snowdonia (Dore et al., 1992; Fowler et al., 1988). To calculate the additional wet deposition in the UK uplands from seeder-feeder scavenging a model of the process is used, as described in NEGTAP (2001) and by Dore et al. (1992). A substantial fraction of wet deposition in UK occurs through the seeder-feeder pathway, as illustrated in Figure 3.6. Table 3.1 shows that for the deposition of sulphur, and oxidized and reduced nitrogen, orographic enhancement of wet deposition contributes 20.9%, 20.5% and 19.5% respectively of the wet deposition over the UK.

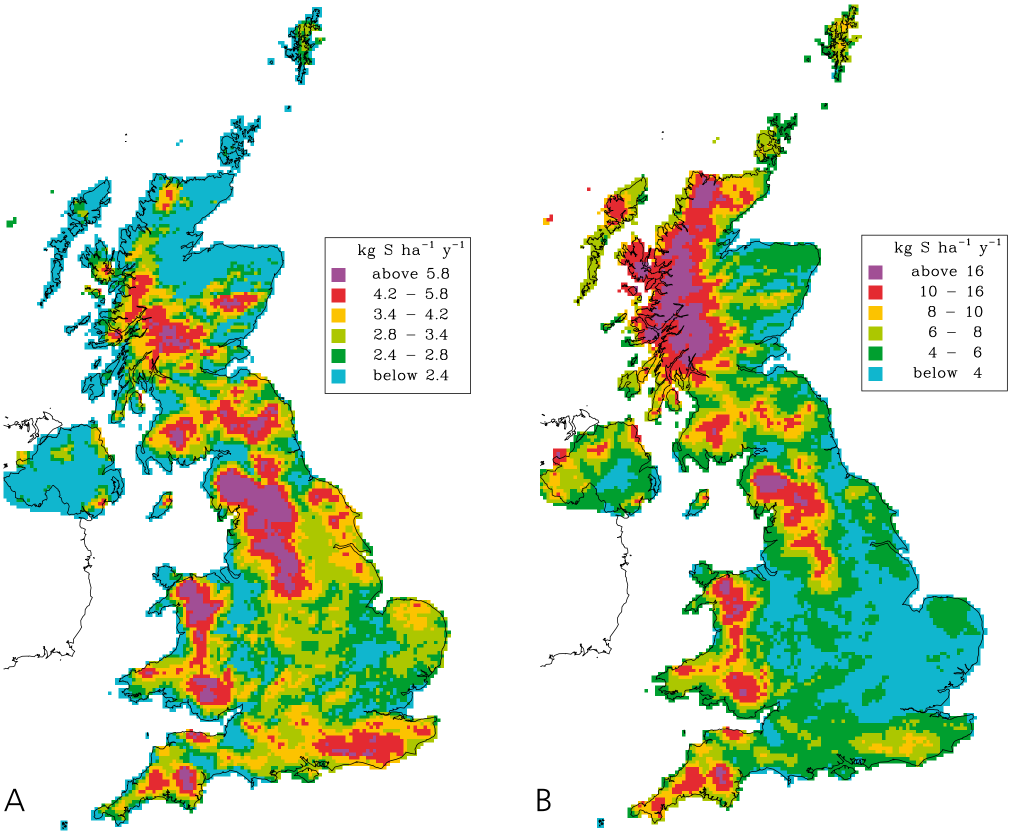


Figure 3.7: Annual wet deposition of (a) non-sea-salt and (b) total wet-deposited sulphur in the UK in 2008 (These maps include precipitation and cloud droplet (occult) deposition.). Figure compiled using data from UKEAP (2010).

The resulting maps of wet sulphur deposition, including occult deposition, for 2008 are shown in Figures 3.7a and 3.7b, representing total and non-sea-salt sulphur respectively. The pattern in wet deposition shows the high deposition area to be primarily in the uplands of the west and north, with peak wet deposition in the range 10-20 kg S ha^{-1} annually. It is notable that in the UK sea-salt is now a substantial fraction of the total, averaging 44% over the country as a whole. Because anthropogenic S deposition in the country has declined since 1986, the sea-salt fraction has become proportionally larger, from 27% of total wet deposition in 1986 to 44% in 2008. The absolute amount of wet sea-salt deposition remained fairly constant between 1986 and 2008 at about 80 Gg-S annually. The current wet deposition of anthropogenic sulphur at 85 kt in 2008 has decreased from 252 Gg-S in 1986, a reduction of approximately 70%. All individual sites in the network show statistically significant reductions in SO_4^{2-} concentrations. The average trend at UK monitoring stations is shown in Figure 3.8. As in the case of acidity there are important regional differences with the largest trends in central and eastern England.

The smallest trends are found at sites in south-west England where sources of sulphur from shipping, which have increased over the last 20 years, have masked decreases in other sources.

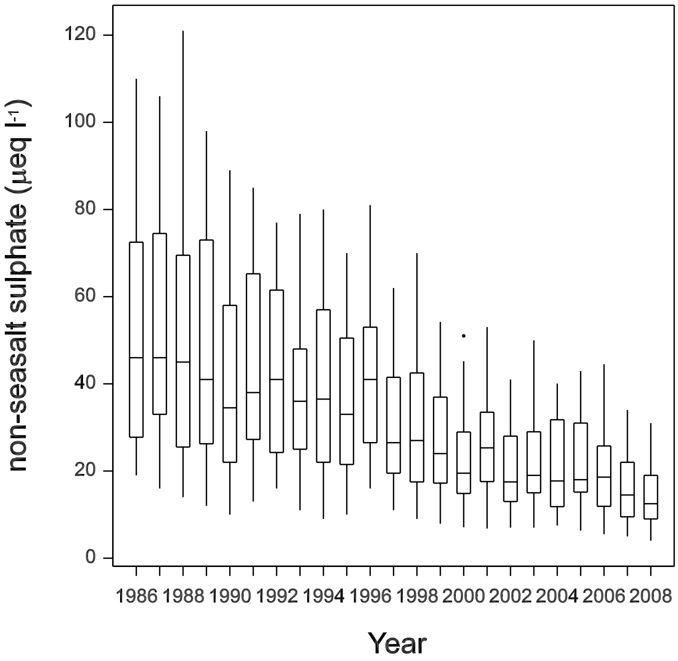
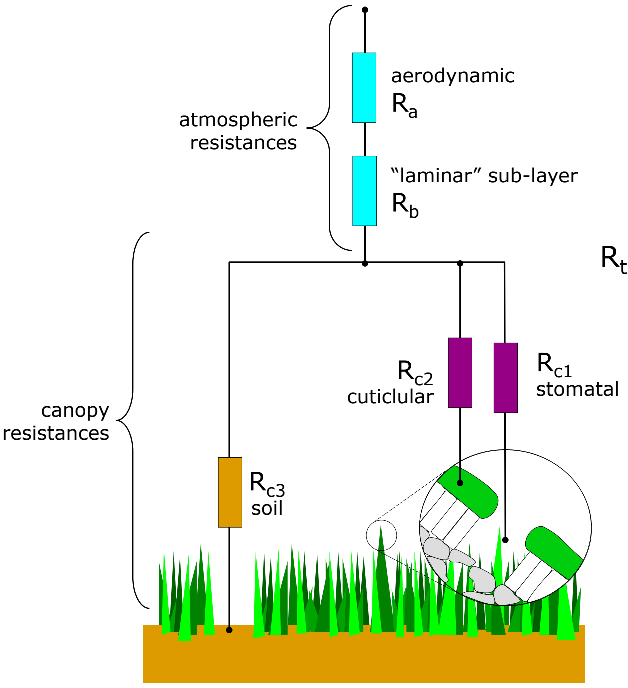


Figure 3.8: The trend in annual non-sea-salt SO_4^{2-} concentrations in precipitation (Each point represents the mean of the precipitation-weighted concentrations for all sites in the UK monitoring network for that year.) Figure compiled using data from UKEAP (2010).

The deposition of sulphur as cloud-water droplets is included in the wet deposition totals and contributes 5% to the total deposition. However, cloud deposition is important at high elevation sites (>600 m above mean sea level), where it contributes substantially to total inputs and is the main mechanism through which vegetation is exposed to potentially damaging concentrations of SO_4^{2-} (Fowler *et al.*, 1991).

3.3.4 Dry deposition

Dry deposition includes the turbulent transfer of gases and aerosols and the gravitational settling of aerosols to the surface. In the case of gaseous SO_2, as the gas is highly reactive and soluble in water, deposition to terrestrial surfaces represents an important removal process for SO_2 in the boundary layer (Garland, 1977) and limits the atmospheric lifetime in the boundary layer to about a day. Rates of deposition are generally expressed as a deposition velocity, (v_g = flux/concentration at a reference height) which is regulated sequentially by rates of turbulent transfer within the atmosphere to the surface and hence wind velocity and the aerodynamic roughness on the surface, and then by the rates of reaction with or solution of SO_2 within materials present at the surface (foliage, bark, soils, water and building materials in the built environment). The process is illustrated in Figure 3.9.



$$R_{total} = R_a + R_b + \left(\frac{1}{R_{c1}} + \frac{1}{R_{c2}} + \frac{1}{R_{c3}}\right)^{-1}$$

$$\frac{\text{Flux}}{\text{Concentration}} = \frac{1}{R_{total}}$$

Figure 3.9: A simple resistance network illustrating the pathway of dry deposition for gases and aerosols.

Rates of SO_2 deposition under field conditions can be measured directly using micrometeorological methods but, except at one or two locations globally, dry deposition is not monitored due to the cost and complexity of the measurements. Instead, campaign data of dry deposition measurements over a range of different surface types have provided the main source of information (Fowler *et al.*, 2009). These data are used to parameterise the components of surface resistance within a dry deposition model, using measured meteorology and SO_2 concentration maps as shown in Figure 3.3 and described by Smith *et al.* (2000). In early work on dry deposition of SO_2 it was assumed that, having obtained representative deposition rates for the countryside and using appropriate meteorology, the process could be modelled into the future with confidence. However, the deposition process has been shown to be mainly controlled by chemical reactions in the moist layers present on vegetation most of the time (Erisman *et al.*, 1998) and as a consequence dry deposition rates change as the chemistry of the atmosphere changes. In particular the ratio of SO_2:NH_3 in surface air controls the pH of the water layer on vegetation and thus the solubility of SO_2, which is very sensitive to pH. Detailed field measurements have demonstrated the underlying process, often referred to as 'co-deposition' (Erisman and Wyers, 1993), and a simple mechanistic model to simulate the overall scheme is described by Flechard *et al.* (1999). The practical consequence of these findings is that as emissions of SO_2 decline, independently of any changes in NH_3, the canopy resistance to SO_2 deposition declines, leading to a steady increase in deposition velocity with time. The theoretical changes are substantial and would lead, in the most polluted areas of Europe to a doubling of deposition velocity between the late 1970s and 2006. There are long-term measurements of SO_2 dry deposition at Auchencorth Moss in Scotland, where the increase in deposition velocity has been measured directly (Fowler *et al.*, 2001). Table 3.2 provides a summary of the temporal trend in deposition velocity with time.

Table 3.2: Annual statistics of the dry deposition measurements of SO_2 at Auchencorth Moss between 1995 and 2006. (Fowler *et al.*, 2009).

	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
SO_2(1m) mg m^{-3}	0.55	0.73	0.52	0.35	0.45	0.39	0.38	0.36	0.53	0.34	0.66	0.42
Flux SO_2 ng m^{-2} s^{-1}	-2.71	-3.27	-3.36	-2.72	-2.63	-2.95	-2.81	-3.17	-3.74	-1.85	-5.98	-2.65
v_d(1m) mm s^{-1}	4.92	4.51	6.42	7.69	5.80	7.55	7.48	8.83	7.10	5.42	9.00	6.37
R_a(1m) s m^{-1}	34.8	34.3	34.2	30.7	30.3	26.1	30.1	28.9	30.1	27.5	31.5	24.1
Rb_{SO2} s m^{-1}	18.4	18.8	18.7	16.8	15.9	17.8	18.0	16.7	17.9	18.5	22.1	21.3
Rc_{SO2} s m^{-1}	150.0	168.5	102.9	82.6	126.2	88.6	85.6	67.7	93.0	138.3	57.5	111.5

Upscaling the dry deposition velocity data to the UK using measured SO_2 concentrations and meteorological data and a process-based model (Smith *et al.*, 2000) provides spatially disaggregated maps for the UK land surface, as shown in Figure 3.10 for 1987, 2001 and 2008. The decline in dry deposition is a very strong feature of the overall sulphur dataset; this is the component within the sulphur budget that changes most, declining from 390 Gg-S yr^{1} in 1986 to 32 Gg-S yr^{1} in 2008, and which is driven by the change in SO_2 concentration. Changes in surface resistance have not been applied to produce these maps as there is insufficient data to define changes in canopy resistance in the period 1986 to 1994, i.e. before continuous monitoring of SO_2 dry deposition.

3.3.5 Trends in sulphur deposition and partitioning between wet and dry deposition

The trends in wet and dry deposition show large reductions in each component, but dry deposition decreases much more rapidly than wet deposition, and considering their relative importance within the overall budget, dry deposition changes from the dominant term (60%) in the late 1980s to the minor term (20%) by 2005 as shown in Figure 3.11. These changes have important consequences on ecological effects, as wet and dry deposition contribute very different fractions of the total sulphur deposition and different chemical forms of the pollutant in different areas of the country.

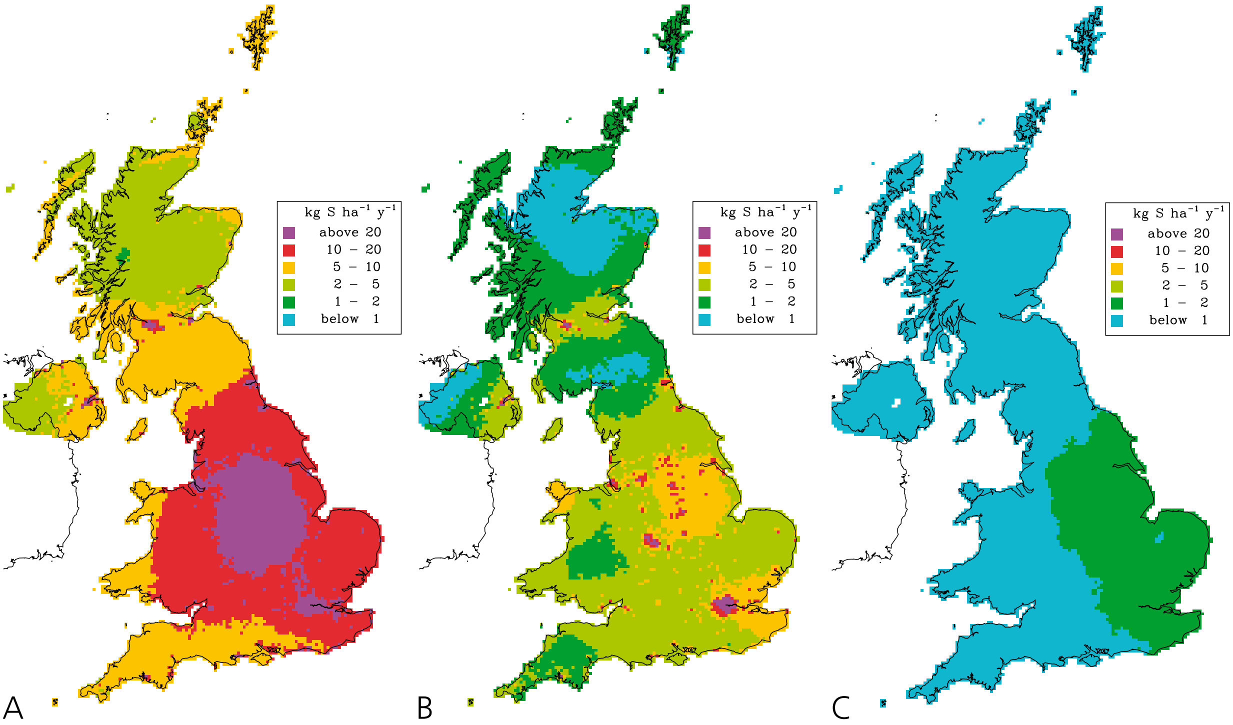


Figure 3.10: Dry deposition of SO_2 in the UK for 1987 (left), 2001 (centre) and 2008 (right), from measured SO_2 concentrations and meteorological data coupled to a process-based model of dry deposition (Smith et al., 2000).

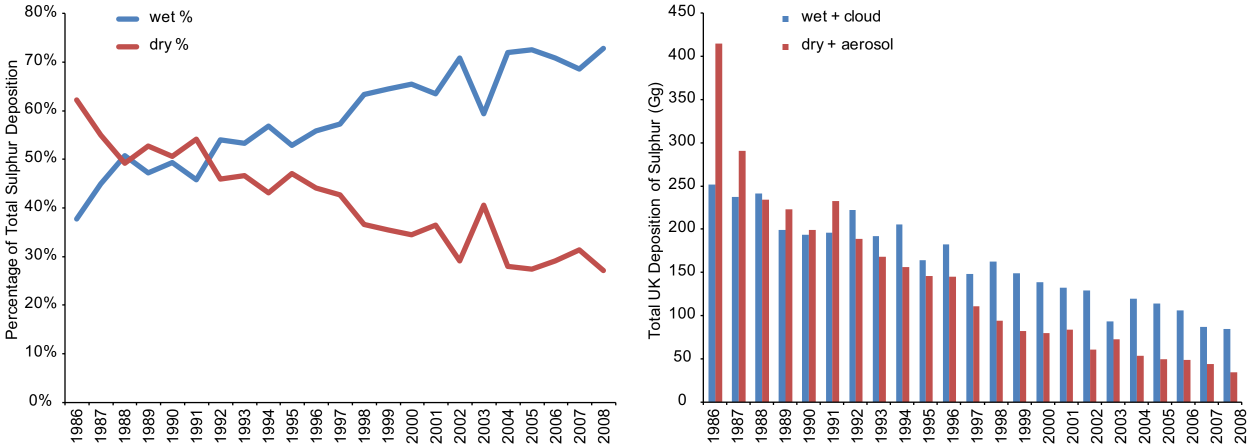


Figure 3.11: The changing relative importance of wet and dry deposition in UK sulphur deposition between 1986 and 2008. Figure compiled using data from UKEAP (2010).

Dry deposition is most important in areas close to the sources of sulphur emission, as shown in the dry deposition maps (Figure 3.10), whereas wet deposition maxima occur in the high rainfall areas of the UK uplands in the north and west of the country (Figure 3.7). The changes in relative contributions of wet and dry deposition result in the greatest benefits in terms of reduced deposition in the lowlands of eastern and central England, close to the sources of SO_2, and the smallest benefits in the high rainfall areas of the west and especially upland UK. The marked change in deposition pathway is illustrated

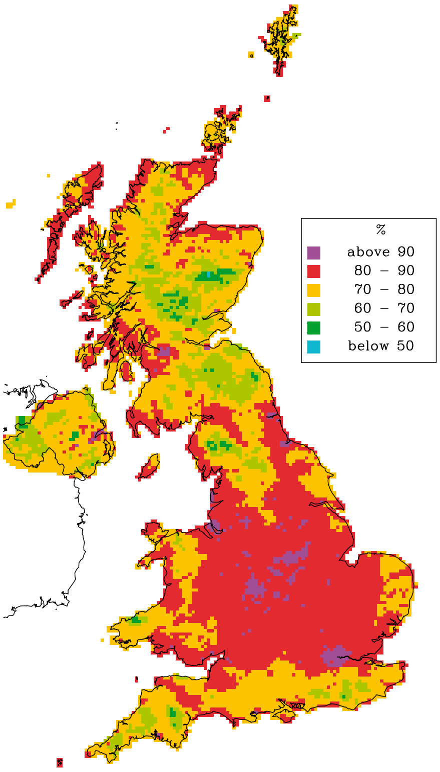


Figure 3.12: The percentage reduction in anthropogenic sulphur deposition between 1987 and 2008 mapped over the UK at 5 km x 5 km resolution Figure compiled using data from UKEAP (2010).

in Figure 3.12, showing the percentage reduction in deposition mapped over the UK. The reductions in sulphur deposition in central and eastern England are very large, in excess of 80%, and represent a very large change in the chemical climate of this region since the 1980s. The high rainfall areas of the country and the regions remote from sources of sulphur have experienced much smaller reductions in deposition, typically 30% to 50%. The ecological consequences of these changes are considered in Chapter 5.

3.3.6 Non-linearities in the emission–deposition relationship

The changes in sulphur deposition are important results of the emission reduction policies adopted by the UK Government progressively from the late 1980s onwards following UNECE protocols and conventions, as described in the introduction. It is clear from the monitoring data that there have been substantial changes in the spatial patterns of sulphur deposition and the magnitude of reduction in deposition across the country. The changes in patterns of sulphur deposition and the partitioning between wet and dry deposition lead to non-linearities in the emission–deposition relationship with respect to a specific area (e.g. the UK), since the reductions in UK (or European) emissions do not cause the same reduction in deposition throughout the UK, or even over the UK as a whole (Fowler *et al.*, 2005). Furthermore, the relationship between emission and deposition within the UK changes with time over the monitoring period, as shown in Figure 3.13. Considering the sulphur budget of the atmosphere over the UK a simple plot of sulphur emissions and deposition within the boundaries of the country reveals an interesting and quite non-linear relationship as in Figure 3.13. In the early 1980s, corresponding to the period in which emissions declined from 200 Gg-S to approximately 1600 Gg-S, the effects of reductions in low level sources from industry and the control of domestic coal burning led to rapid decreases in ambient SO_2 concentrations and a rapid reduction in dry deposition. In fact, the relationship between reductions in emission and deposition within the country during this period were closely coupled, with deposition decreasing by 81% of the emission reduction. In this period most of the benefits of emission reduction were being seen within the country.

In the second part of the dataset, during which time emissions declined by a factor of two from 1600 Gg-S to 800 Gg–S, corresponding to the period 1993 to 1998, deposition within the UK declined slowly from 350 Gg-S to 259 Gg-S, so only 15% of the reduction

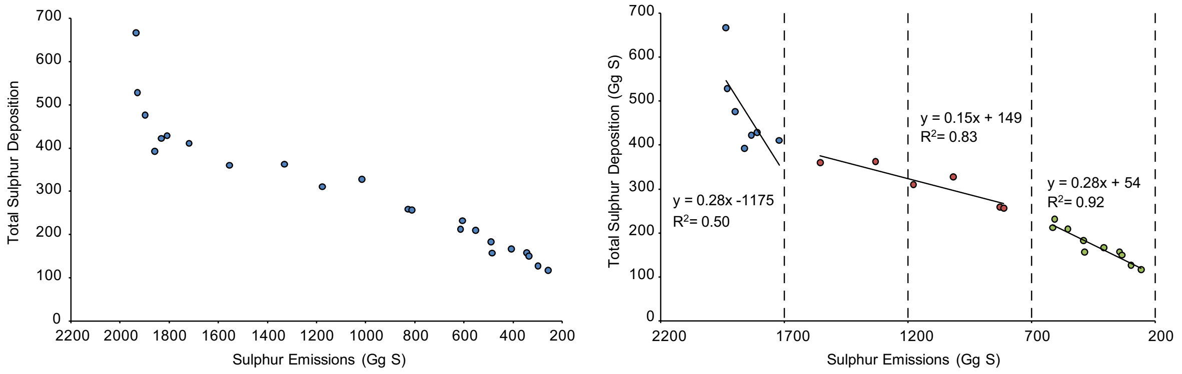


Figure 3.13: The non-linearity in the relationship between sulphur emission and deposition in the UK over the period 1986 to 2008. Figure compiled using data from UKEAP (2010) and the NAEI (Murrells *et al.*, 2010).

in emission was reflected in reduced deposition within the UK during this period. This was the period of fuel switching by the power stations from coal to gas, and the reduction mainly reflects reduced large combustion plant emissions and is a strong indicator of the earlier importance of these sources in the export fluxes of sulphur to Scandinavia. The final phase of the emission reduction from 800 Gg-S to 400 Gg-S corresponds to the period 1998 until 2008 and is the period during which dry deposition and oxidation rates of SO_2 increased in response to the changing ratio of SO_2 and NH_3 in the boundary layer.

Over the 20 years of operation of the monitoring network the fraction of sulphur emissions deposited within the UK has gradually increased, from 27% in 1987 to 45% in 2008 as shown in Figure 3.14.

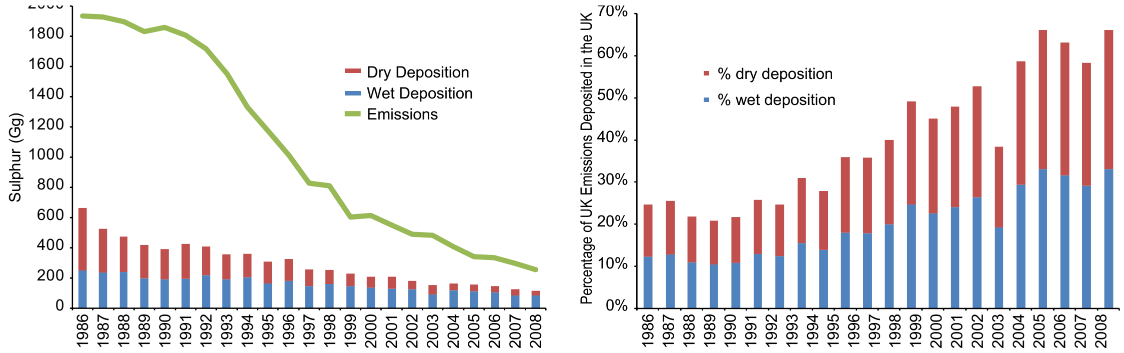


Figure 3.14: The temporal trend in sulphur deposition in the UK showing the fraction of UK emissions deposited within the country between 1986 and 2008. Figure compiled using data from UKEAP (2010) and the NAEI (Murrells *et al.*, 2010).

The atmospheric lifetime of sulphur emissions in the UK has declined over the last 20 years, in response to changes in the oxidation and scavenging processes as a consequence of altered boundary layer atmospheric chemistry and composition.

Another important characteristic of the changing fate of UK emissions is the lifetime of sulphur compounds in the atmosphere. As transformation rates of the primary SO_2 emission to SO_4^{2-} and deposition rates have increased, then the atmospheric lifetime and footprint of UK emissions have decreased. The average UK data may be used to calculate the change in atmospheric lifetime (defined as the ratio of the mass in the atmosphere to the removal rate). Assuming the climate over the UK has remained constant over this 20-year period, the measurements show that the average lifetime of sulphur in the UK in 1990 was 14 hours and had declined to 6 hours in 2005. These lifetimes correspond to an average travel distance in the atmosphere of 500 km in 1990 and 200 km in 2005.

These changes in processing of sulphur compounds in the atmosphere over the UK have important policy implications and show that the clean-up of the atmosphere has proceeded more rapidly than was expected. The atmospheric sulphur budget over the UK is shown schematically in Figure 3.15 to illustrate the main changes between 1987 and 2008.

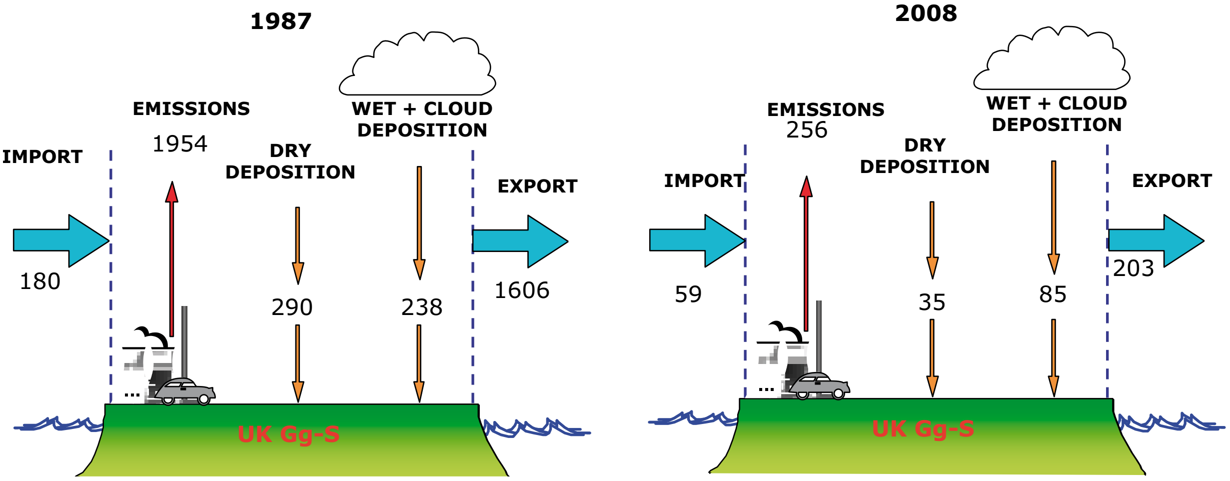


Figure 3.15: The atmospheric budget for non-sea -salt sulphur (all units Gg-S) over the UK in 1987 and 2008. Figure compiled using deposition data from UKEAP (2010), emission data from the NAEI (Murrells *et al.*, 2010), and outputs from CBED and EMEP models.

3.4 Nitrogen deposition in the UK

Unlike sulphur compounds, a consideration of fixed atmospheric nitrogen requires measurements of a wide range of different gaseous species, including NO, NO_2, HNO_3, nitrous acid (HONO), NH_3, and PAN (peroxyacetyl nitrate) and related acetyl nitrates (Monks *et al.*, 2009). There are in addition many organic nitrogen species present in the atmosphere, but while their presence has been noted (Cape *et al.*, 2004), no satisfactory networks to define their contribution to nitrogen deposition in the UK have been established. It is also important to stress the relative importance of oxidised and reduced nitrogen within the deposition budget, as these derive mainly from different industrial sectors, have different atmospheric lifetimes and require different control measures for effective abatement. An important conclusion of the NEGTAP (2001) analysis was that nitrogen deposition in the UK was dominated by reduced nitrogen as dry-deposited NH_3 and aerosol NH_4^+, and in 1997, 57% of total nitrogen (N) deposition in the UK was believed to be due to reduced N compounds (NEGTAP, 2001). However, at that time HNO_3 was not included in the budget as measurements had only just begun. Since the publication of NEGTAP (2001), a network of HNO_3 and aerosol samplers throughout the UK has been established to provide the necessary data to calculate dry deposition of these nitrogen compounds. The synthesis of these data significantly updates the NEGTAP analysis. In particular the deposition of oxidised nitrogen is now known to be substantially larger, as it now includes nitric acid and aerosol N deposition. There have also been advances in quantifying reduced nitrogen deposition which have led to reductions in the estimates of dry deposition of NH_3 to vegetation, which has thus reduced deposition estimates for the whole country. There have also been substantial reductions in estimates of emissions of oxidised nitrogen and smaller reductions in ammonia emission estimates.

3.5 Oxidised nitrogen

3.5.1 Oxidised nitrogen concentrations in the UK

The main compounds of oxidised nitrogen include the nitric oxide (NO), nitrogen dioxide (NO_2), nitrous acid (HONO) and nitric acid (HNO_3). Other minor components which are

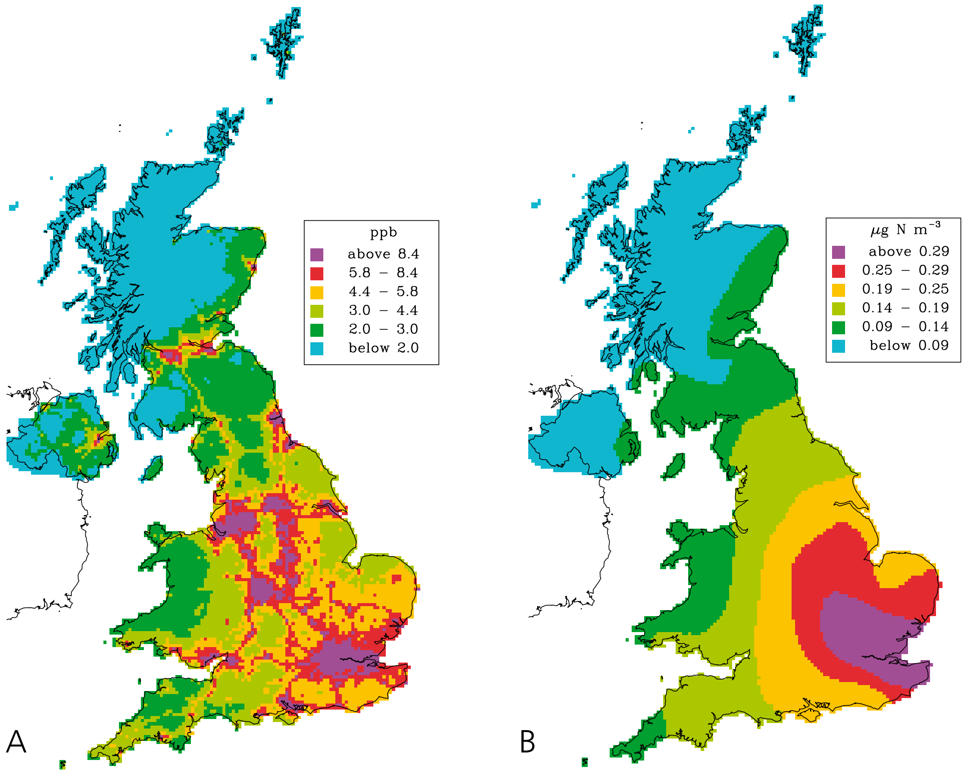


Figure 3.16: (a) Ambient NO_2 and (b) HNO_3 concentrations in the UK in 2008 (The mapped HNO_3 values were interpolated directly from the mainly rural measurements, the NO_2 values were derived from a combination of modelling (to quantify the values close to roads and urban areas) and an interpolated field of the rural measured values.) Figure compiled using data from UKEAP (2010).

not routinely measured in the UK include peroxyacetyl nitrates (e.g. peroxyacetyl nitrate $CH_3COOONO_2$). Oxidised nitrogen is also present as nitrate (NO_3^-) in aerosols, cloud and rain. The monitoring networks provide measured concentration fields for NO_2 from trace gas analysers and diffusion tube samplers in rural and urban networks (http://www.uk-pollutantdeposition.ceh.ac.uk/image/tid/7) and HNO_3 measurements from the Delta sampler network. As NO is short-lived in the atmosphere and is not deposited to the surface at significant rates, there are no national measurement networks for this species. NO_2 measurements throughout the UK in rural areas are available for most of the last 20 years, and provide national coverage.

The measured NO_2 concentrations (Figure 3.16a) highlight the predominance of traffic and urban sources, with the largest concentrations in the large conurbations and adjacent to the motorway network, with annual mean concentrations in excess of 10 ppb in these areas. It is notable that there is a considerable excess of NO_2 over SO_2 often by more than an order of magnitude, and this contrasts with the values in and around the urban centres where SO_2 was generally the dominant gaseous pollutant in the 1960s and 1970s.

The concentration field for HNO_3 (Figure 3.16b) shows a much smoother field than NO_2, reflecting the secondary nature of HNO_3. However, the network is relatively small, with just 30 UK sites; in practice the concentration field would show greater spatial variability, due to factors which influence the turbulent deposition of HNO_3 to the surface and thus local depletion of the surface concentration, if sufficient sites were available. The largest concentrations are found in south-east England with peak annual average values of 0.4 µg-N m^{-3}, about an order of magnitude smaller than NO_2 concentrations. In the west and north of the UK, HNO_3 concentrations are much smaller, and typically below 0.1 µg-N m^{-3}.

Aerosol NO_3^- concentrations have been measured along with HNO_3 in the Delta denuder network for the last 8 years, providing a robust dataset for analysis and the beginnings of a longer-term monitoring record. Figure 3.17 shows the annual aerosol NO_3^- concentration field for the UK along with the average concentration of NO_3^- in rain, weighted for volume. These maps show broad similarities but with the area of maximum concentration for aerosol being further south than that for NO_3^- in rain.

3.5.2 Deposition of oxidised nitrogen

The dry deposition rates of gaseous NO_2, HNO_3 and aerosol NO_3^- (see Figure 3,18) are calculated from the measured concentration fields using the resistance model described for SO_2 but with surface resistance formulations for the respective gases and aerosol species (Smith *et al.*, 2000). The deposition rates of HNO_3 are large due to its reactivity with natural surfaces and solubility (Huebert and Robert, 1985) and, even with relatively small ambient concentrations, countrywide deposition is substantial, with values typically 60 Gg-N yr^1 and of a similar magnitude to wet deposition of NO_3^- but larger with warm summers, such as 2003 (87 Gg HNO_3-N). The pattern of dry deposition follows the concentration field, but is modified by topography and land use. The very small surface resistance makes HNO_3 deposition very sensitive to the aerodynamic roughness of terrestrial surfaces, and as a consequence forests are an important sink for $HNO_{3;}$ the major forests in the deposition map (Figure 3.18a) are readily identified (e.g. Thetford,

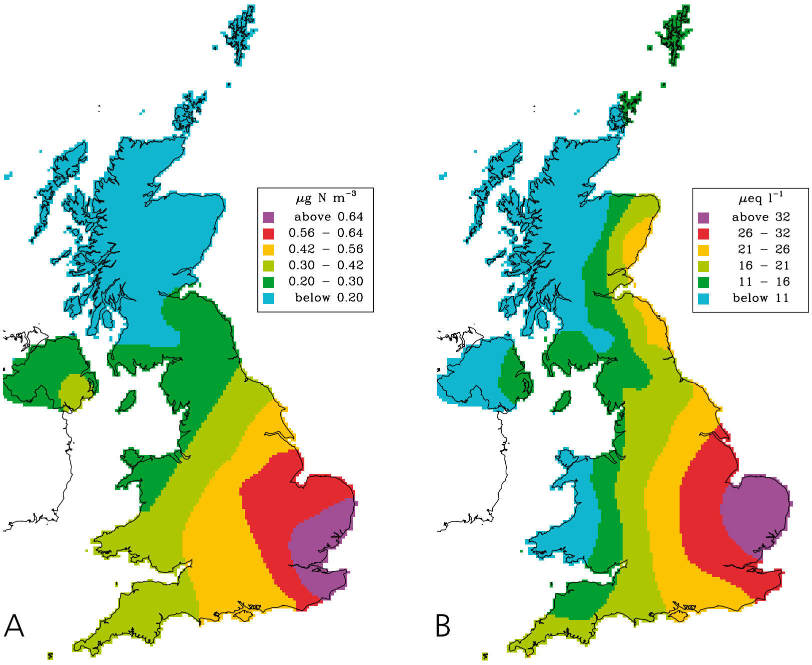


Figure 3.17: Annual average measured concentrations of (a) aerosol NO_3^- and (b) volume-weighted concentrations of NO_3^- in precipitation in 2008. Figure compiled using data from UKEAP (2010).

New Forest, Kielder, etc.). Woodland and hedgerows are sites of enhanced N deposition through capture of HNO_3. The deposition modelling captures most of the processes and spatial features, but peaks in deposition would also be expected in areas of enhanced wind speed, ridges and exposed hill summits, but much of this fine structure is not evident as a consequence of the spatial resolution of the modelling, however it is very likely that these areas are hot spots for HNO_3 deposition.

Dry deposition of NO_2 (Figure 3.18b) follows the concentration field closely and is largest in urban areas and close to the motorways. Aerosol NO_3^- deposition (Figure 3.18c) provides a small contribution to the total nitrogen deposition and is largest for woodland and in the south-east of the country.

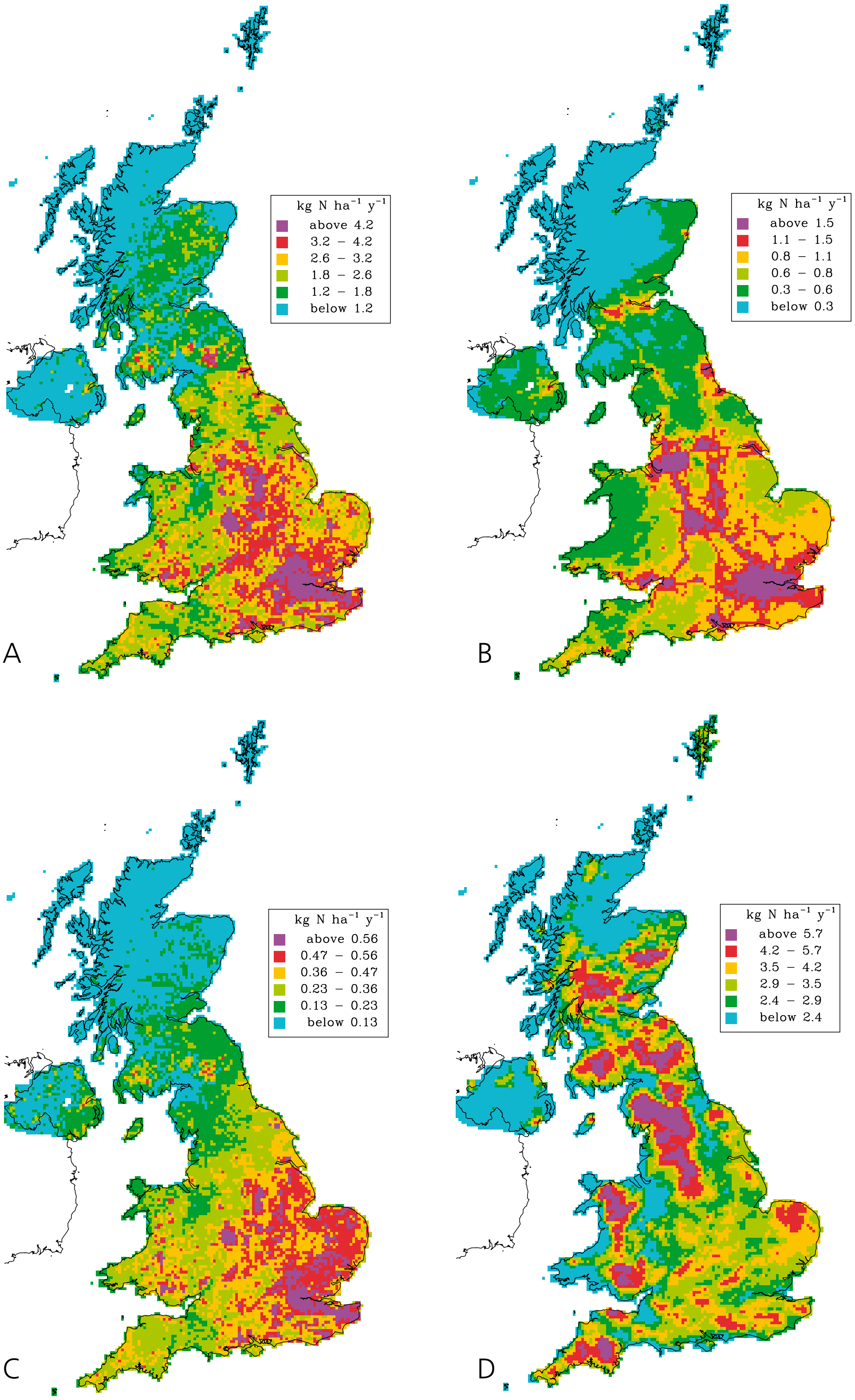


Figure 3.18: Annual dry deposition of (a) HNO_3, (b) NO_2, (c) aerosol NO_3^- and (d) wet deposition of NO_3^- in the UK in 2008 (Compiled using data from UKEAP (2010) and deposition rates derived from models described by Smith et al. (2000) and NEGTAP (2001).

3.5.3 Trends in oxidised nitrogen in the UK

The 50% decline in UK emissions of NO_2 since establishment of the wet deposition network in 1986 provides a substantial signal to test the relationship between emission and deposition within the boundaries of the UK. NO_2 data over the country as a whole show a decline in ambient concentration of ~50% over the 20 years, entirely consistent with the change in emissions, as shown in Figure 3.19.

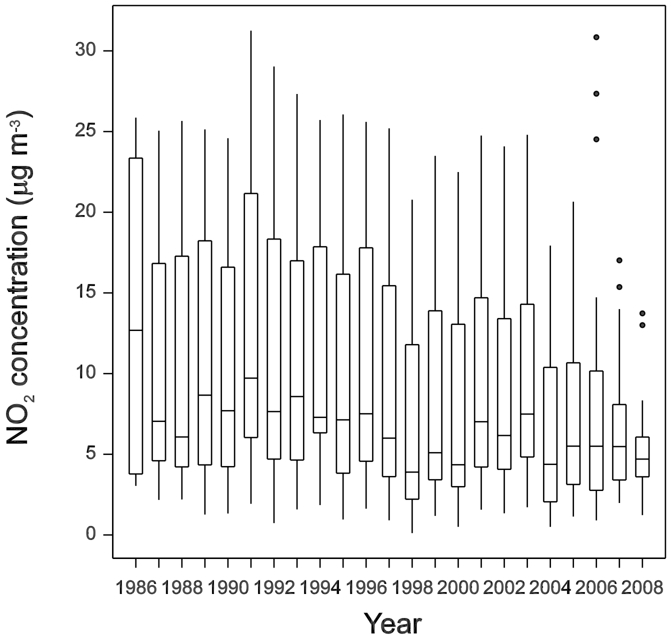


Figure 3.19: The trend in rural NO_2 annual mean concentration measurements in the UK between 1986 and 2008. Figure compiled using data from UKEAP (2010)

Table 3.3: The trend in concentrations of NO_3^- in precipitation over rural UK between 1986 and 2006 (calculated using data from UKEAP (2010)).

Site	Slope	y-intercept	% decline	p-value
Bottesford	-2.95	90.2	62.1	0.000
Compton	-2.38	99.0	45.7	0.016
Driby	-1.86	115	30.7	0.038
Flatford Mill	-1.47	91.5	30.5	0.005
Hillsborough Forest	-2.27	133	32.4	0.039
Llyn Llydaw	-4.72	113.8 (in 1997)	33.4 (since 1997)	0.020
Lough Navar	-6.28	249	47.9	0.019
Preston Montford	-3.21	106	57.5	0.029
Redesdale	-1.87	98.3	35.0	0.015
Stoke Ferry	-1.49	82.2	34.4	0.005
Thorganby	-5.83	151	73.4	0.000
Wardlow Hay Cop	-3.15	125	47.9	0.013
Woburn	-1.84	77.5	45.1	0.004

When the data for wet deposition are examined a statistically significant reduction in concentration is observed over the 20-year monitoring period. The reduction in concentration and deposition amounts to ~24% over the period 1986-2008 as shown in Figure 3.20 and in Table 3.3, the same period over which emissions declined by 50%. There are decreases in concentration at some of the individual sites.

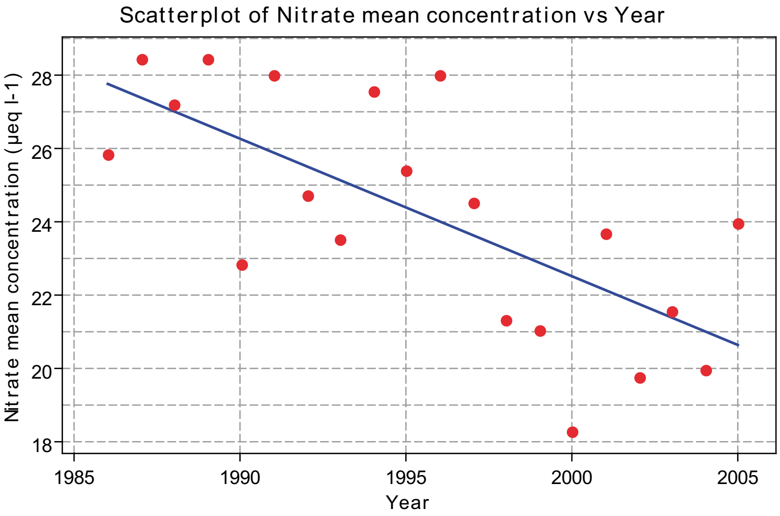


Figure 3.20: The trend in rainfall NO_3^- concentration averaged annually over all network stations in the UK during the period 1986 to 2006 (showing a 22% reduction over 20 years). Source: RoTAP.

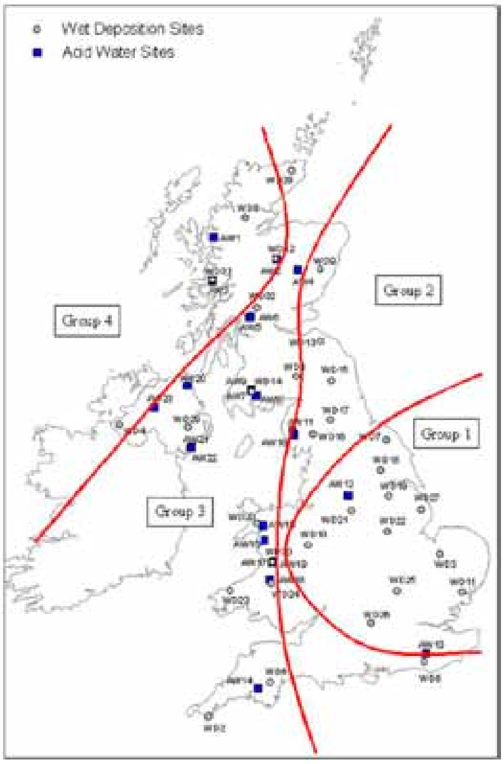


Figure 3.21: The classification of areas of the UK by the trends in rainfall acidity, showing four regions in which statistically consistent trends are observed (NEGTAP, 2001).

From the individual site analysis, 13 sites have statistically significant negative trends; 10 of these are in the source area shown in Figure 3.21 as Group 1: Preston Montford, Wardlow Hay Cop, Compton, Thorganby, Bottesford, Jenny Hurn, Woburn, Driby, Stoke Ferry and Flatford Mill. The only site in Group 1 not to record a significant negative trend was High Muffles. Two more sites with significant trends are located in Group 2 (Hillsborough Forest and Redesdale) and the other is in Group 4 (Lough Navar).

From the regression analysis, there is sufficient evidence to suggest that the negative trend for nitrate over time is highly significant, indicated by the *p*-value in the analysis of variance (Table 3.3). The *r*-squared value for the data is small, an indicator of the scales of variability relative to the temporal trend.

The reduction in wet deposition of NO_3^- is approximately 24% between 1986 to 2008 over the UK as a whole. The 24% reduction in rainfall NO_3^- concentration (and wet deposition) is approximately half of the 50% decline in emissions over the 20 years. Thus, as in the case of sulphur, the emission–deposition relationship shows important non-linearities. The NO_2 concentration has declined at almost the same rate as the reduction in emissions, and precipitation amounts have not changed significantly over the monitoring period, which suggests that uncertainties in the emission data and meteorology changes are not likely to be the cause of the non-linearity. It is probable therefore that changes in chemical processing of NO_x emissions in the atmosphere are responsible for the observed non-linearity. The overall changes in the oxidised nitrogen budget are summarised in Figure 3.22.

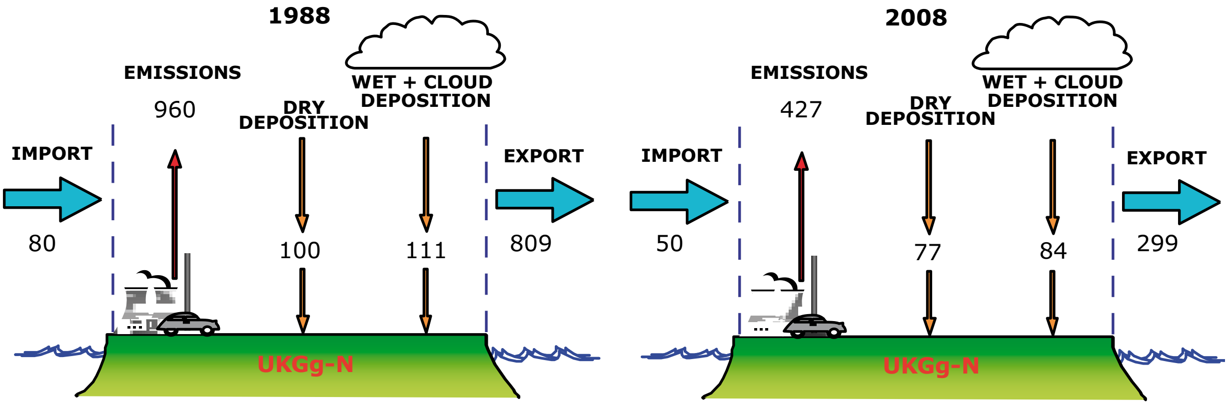


Figure 3.22: A comparison of the atmospheric budget for oxidised nitrogen over the UK in 1988 and 2008 showing the main response to reductions in emissions to be the decline in export of NO2 from the UK. Figure compiled using deposition data from UKEAP (2010), emision data from the NAEI (Murrells *et al.*, 2010), and outputs from CBED and EMEP models.

The UK monitoring of nitrogen compounds has improved over the last 20 years. In the early years measurements were restricted to precipitation chemistry, followed by the introduction of rural NO_2 measurements in 1995, and aerosol NO_3^- and HNO_3 measurement networks in 2000. Thus it is now possible to calculate directly from measurement-based concentration fields the deposition of these components of the oxidised nitrogen budget in the atmosphere over the UK. To provide an estimate of the temporal changes in the budget since the early precipitation chemistry measurements, dry deposition of NO_2 was assumed to be proportional to emissions and aerosol NO_3^- and HNO_3 remained constant at 10 Gg and 60 Gg respectively between 1988 and 1999. In support of this assumption precipitation scavenges mainly the aerosol and HNO_3, and concentrations of NO_3^- in rain over most of the UK remained fairly constant between 1988 and 1999. With these assumptions the mass budget for oxidised nitrogen in Figure 3.22 provides an illustration of the main changes in emission deposition and export, showing that the main result of the reduction in emissions is a reduction in the export of oxidised nitrogen from the UK, which has declined by 62% in 20 years, while deposition within the UK has declined by only 24%. If HNO_3 and aerosol NO_3^- had changed substantially, it would have been reflected in the NO_3^- in precipitation and wet deposition, which has changed little (-24%) relative to changes in emissions (-55%).

3.6 Reduced nitrogen

Reduced nitrogen comprises mainly gaseous NH_3, aerosol NH_4^+ and wet deposited NH_4^+ which are monitored throughout the UK in the wet and dry deposition networks. Other reduced nitrogen species, including amines and other organic compounds, are not widely measured. For wet deposition, water-soluble organic N contributes 24-40% of total N deposition in bulk rainfall collected at a range of UK locations (Cape *et al.,* 2004). While it is not clear how much of this was dry deposited on collectors (Benitez *et al.*, 2009), the presence of significant amounts of water-soluble organic N in both the gas and aerosol phase suggests that dry deposition of organic N may also contribute a significant fraction of the total (Benitez *et al.*, 2010). The chemical composition and sources of atmospheric organic N are not known sufficiently well to include these compounds in the UK atmospheric N budget (Ozel *et al.*, 2010).

3.6.1 Concentrations of NH_3 in the UK

Monitoring networks for gaseous NH_3 have been operating continuously since 1998. Concentrations show large spatial variability, reflecting a combination of the large number of ground level sources, primarily related to livestock farming, and the very reactive nature of gaseous NH_3. Figure 3.23 shows the NH_3 concentration field for the UK, mapped using the FRAME model and calibrated using the measured NH_3 values at monitoring stations.

Concentrations of NH_3 range from 10 $\mu g\ m^{-3}$ in areas of intensive livestock production, especially dairy and beef production, to 0.1 $\mu g\ m^{-3}$ in the Scottish Highlands, especially in the north-west of Scotland and in the Hebrides. The concentrations of aerosol NH_4^+, like those of NO_3^- or SO_4^{2-}, show a much smoother field, with the largest values in central and eastern England and the smallest values in north-west Scotland. The dry and wet deposition of reduced nitrogen follow the same methodology as for SO_2 or NO_2, except that in the case of NH_3 the dry deposition process is complicated by the fact that vegetation and soil can be either a source or a sink for atmospheric NH_3, depending

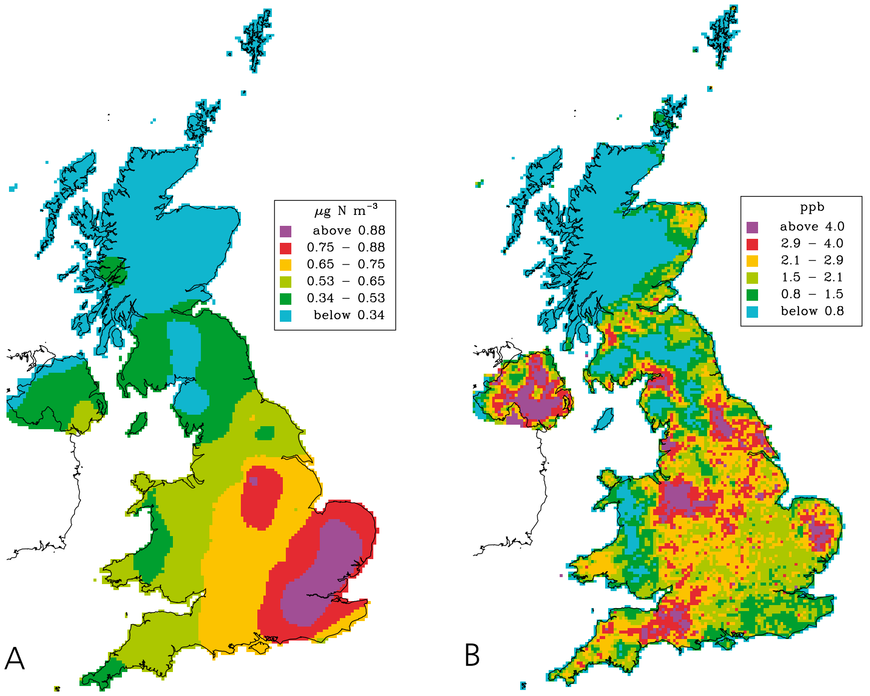


Figure 3.23: Annual average measured (a) particulate NH_4^+ concentrations and (b) gaseous NH3 concentrations modelled using the FRAME model for 2006 (Dore *et al*., 2007).

on the relative magnitudes of the ambient NH_3 concentration and the equilibrium NH_3 concentration within the apoplast of vegetation (Sutton *et al*., 1995). Both concentration and deposition maps of NH_3 are provided by the FRAME model (see Chapter 4), following calibration with the measured NH_3 concentrations in the UK network. It is necessary to use modelled values as interpolated concentration fields from the measurement sites, even with in excess of 100 monitoring stations, fail to capture peak values close to the major sources. The mean annual concentrations for gaseous NH_3 (from FRAME) and particulate NH_4^+ (interpolated directly from the measurement sites) are provided in Figure 3.23. The much smoother concentration field for particulate NH_4^+ reflects the secondary nature of this pollutant, while the patchy NH_3 concentration field reflects the nature of the sources in the UK countryside and the short lifetime of gaseous NH_3. It is important to note that the dominant source of NH_3 varies considerably around the country with poultry and pig farming dominating sources in the east and beef and dairy dominating sources in the west (Dragosits *et al*., 1998); see also Figure 2.11b.

3.6.2 Trends in reduced nitrogen

Emissions of NH_3 in the UK peaked in the 1980s and have decreased by about 15% since then, so relative to trends in emissions of SO_2 or NO_x, the decline in NH_3 emissions is small. However, there have been important changes in individual NH_3 sources during the last 10 years, notably as a consequence of the foot and mouth outbreak in 2001. During this period, some areas of the UK experienced sharp declines in the beef and sheep population, especially Cumbria, and the changes were shown to influence ambient concentrations of NH_3 (Sutton *et al*., 2006). Measured concentrations from network sites show a small increase in ambient NH_3 in remote regions and a small decrease in NH_3 in the regions in which pig and poultry emissions dominate the sources (Tang *et al.*, 2009). Other than these changes, which certainly influence regional concentrations and deposition, ambient NH_3 concentrations have changed little over the timescale of the monitoring and no country-scale trends are detectable in the overall dataset from 10 years monitoring. A small trend is however detectable from the rainfall composition measurements over 20 years (Figure 3.24).

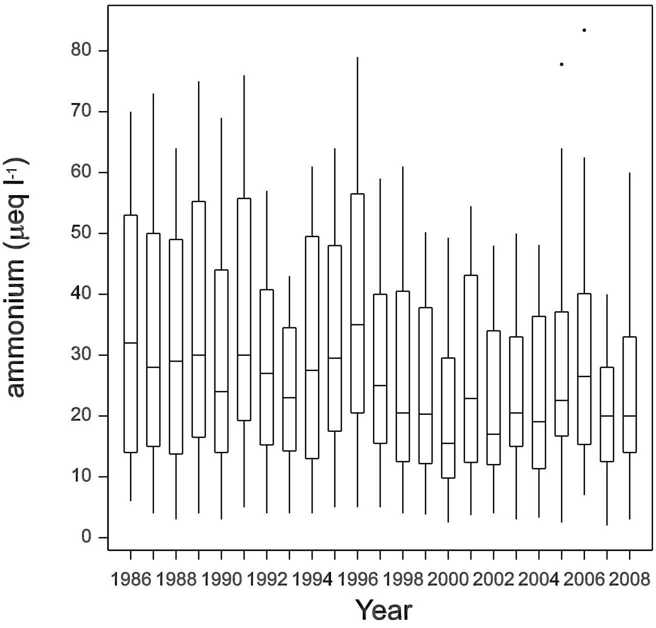


Figure 3.24: Changes in ammonium concentration in precipitation averaged over all sites in the UK network between 1986 and 2008. Compiled using measured concentration data from UKEAP (2010).

From the regression analysis on the data from all sites (excluding new sites with short runs of data), a significant negative trend of -0.615 μeq l^{-1} yr^{1} is observed. The data, however, have a very low correlation, denoted by the *r*-squared value (explaining only 4.0% of the variance). Based on this regression, ammonium in precipitation across the UK decreased by 12.3 μeq l^{-1}, from 1986 to 2005. This equates to an approximate 35% decline in ammonium across the UK as a whole for the same period. However, given the scale of variability in the data, especially in the early years, the magnitude of the trend should be treated with caution.

The measured concentrations of NH_4^+ expressed as a box-plot (Figure 3.24) show the interquartile ranges declining with time, as has the spread of all the data. A large outlier of 124 μeq l^{-1} was identified in 1991, observed at Thorganby, which also recorded the highest annual means out of all the sites in 1990 and 1992.

The data shown in Figure 3.25 illustrate the annual atmospheric budgets for reduced nitrogen for the first year of operation of the NH_3 monitoring network (1997), thus

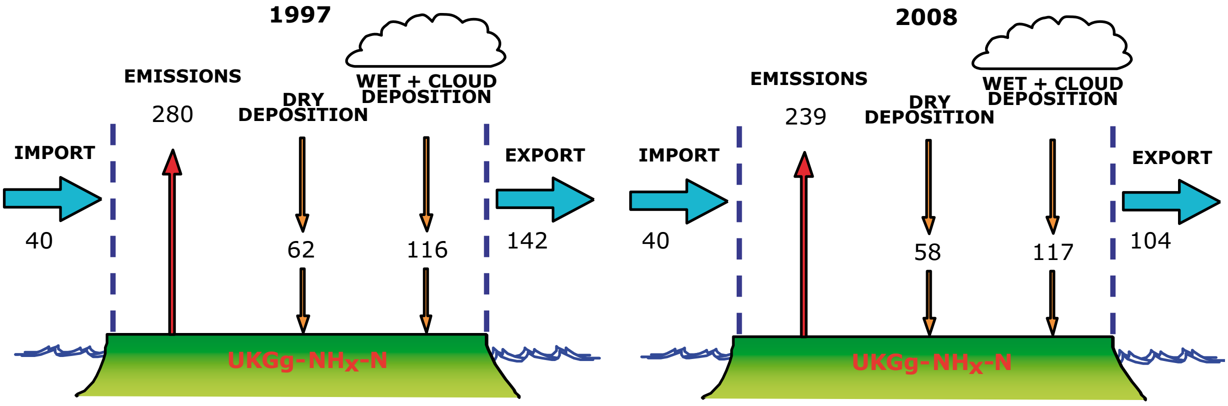
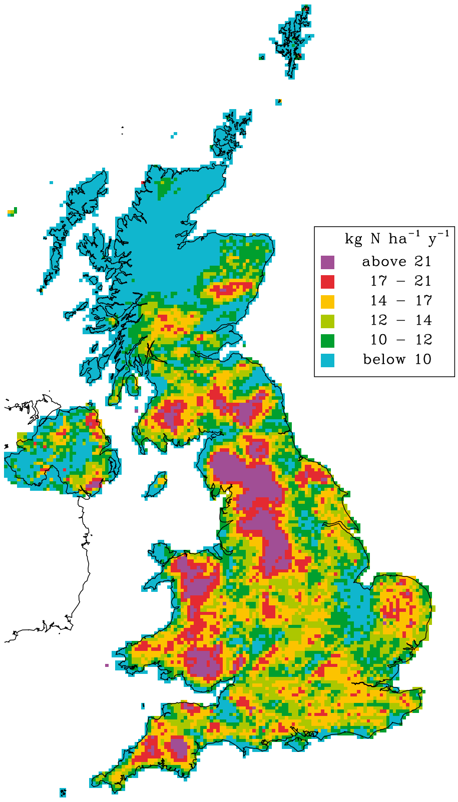


Figure 3.25: The annual atmospheric mass budget for reduced nitrogen for 1997 (the first year in which the UK NH_3 monitoring network operated) and for 2008. Figure compiled using deposition data from UKEAP (2010), emision data from the NAEI (Murrells *et al.*, 2010), and outputs from CBED and EMEP models.

Figure 3.26 Total (oxidised + reduced) deposition of fixed nitrogen over the UK in 2008. Figure compiled using deposition data from UKEAP (2010).



allowing a good estimate of country-scale dry deposition, and also for 2006, the most recent year in which all terms in the budget are available. The data show that almost three-quarters of UK emissions of reduced nitrogen are deposited within the country, consistent with the relatively short atmospheric lifetime of ammonia. Exports represent just over 40% of emissions and imports to the UK from elsewhere in Europe represent about 25% of reduced N deposition in the country (EMEP/EEA, 2009). The two panels in Figure 3.25 show negligible changes in reduced N deposition and only small changes in the overall budget over the UK relative to those for sulphur and oxidised nitrogen, but the time period over which it is possible to construct a robust budget is much shorter for reduced nitrogen.

3.7 Total nitrogen deposition in the UK

The total deposition of nitrogen in the UK in 2008 is shown in Figure 3.26. The figure shows total N deposition is fairly evenly divided between reduced (175 Gg-N yr^{-1}) and oxidised forms (178 Gg-N yr^{-1}). The knowledge of nitrogen deposition in the UK has advanced from that presented in NEGTAP (2001); new monitoring networks for HNO_3 and aerosol NO_3^- and NH_4^+ have allowed more of the components of N deposition to be quantified directly. The ~80 Gg-N of HNO_3 within the deposition budget has changed the overall perception of N deposition, so that the oxidised and reduced forms are equally important in the overall budget of the country. However, the relative importance of reduced and oxidised nitrogen varies considerably across the UK landscape, with reduced N being more important in rural areas, especially in areas of intensive livestock production, while oxidised N is more important in urban areas and close to roads.

The annual total deposition of nitrogen of all forms in the UK is 363 Gg-N yr^{-1} (fairly evenly partioned between oxidised and reduced forms), averaged between 2000 and 2008. The measured deposition since the year 2000 shows inter-year variability of ±30 Gg-N yr^{-1} around the mean of 363 Gg-N yr^{-1} with no overall trend. Earlier years, back to 1987, lack HNO_3, and/or the gaseous NH_3 and ammonia aerosol components needed for a complete budget. Emissions of NH_3 and NO_x were larger in early years and oxidation rates for NO_x to NO_y were probably slower, thus in the absence of direct measurements, the most likely changes in the budget would combine some increases and some decreases of the components with little overall trend in the total. The annual deposition of reactive nitrogen to the UK landscape is large relative to pre-industrial values, and even by comparison with annual fertiliser use in the UK (950 Gg-N yr^{-1}), these deposition values are substantial. A chronology of nitrogen deposition for the UK for the 20th century was constructed by Fowler *et al.* (2004). The effects of deposited nitrogen on soils, vegetation and freshwaters are considered in Chapter 5. The fate of deposited N is potentially an important issue. Evidence to date shows leaching of nitrate in some high deposition areas and elevated NO and N_2O emissions, but relative to the quantities deposited, leaching and gaseous losses are small. The other loss from the system is denitrification to molecular nitrogen (N_2), which is highly uncertain, due to difficulty in measuring this term and the likely scale of spatial variability, this term therefore remains unknown. It seems probable that over much of the semi-natural landscape of the UK, deposited nitrogen is accumulating in soils and vegetation but there is no empirical evidence to support this hypothesis.

3.8 High resolution (1 km x 1 km) maps of pollutant concentrations and deposition in the UK

The maps of concentration and deposition presented so far in this chapter have been at a spatial resolution of 5 km x 5 km, for which maps of the major deposited species are available for the period supported by the measurement networks (1986-2008). The gradual improvement in monitoring techniques over this period has allowed expansion in the number of gaseous and particulate species monitored, and in turn has brought detailed maps of additional species, including NH_3 from 1997 and inorganic aerosol and HNO_3 concentrations from 1999. Component-specific maps derived from measurements are therefore available for different periods of time and these may be obtained directly from the archives of pollutant concentration and deposition data (UKEAP, 2010).

Applications of the deposition data include the policy requirement to demonstrate responses to changes in emissions, especially in quantifying the fate of UK emissions (as above) and the regional distributions in concentration and deposition. However, the terrestrial effects and exceedances of thresholds for effects on specific targets (described in Chapter 5) are an important application of the data; the spatial resolution of the deposition data influences the degree to which assessments of effects can be resolved spatially. In particular, as the fine scale of the concentration and deposition structure is revealed, the number of peaks in the spatial field increases. These peaks arise through proximity to sources of pollutants (e.g. NH_3) and to features of the landscape which cause deposition inputs to be enhanced, for example, through increasing dry deposition by enhancing turbulence (by trees or buildings), or through topographic effects which increase wet deposition, mainly through seeder-feeder scavenging, and dry deposition through increases in turbulence.

To estimate the exceedance of pollutant deposition or exposure thresholds, it is necessary to associate spatially disaggregated land use information with the pollutant exposure or input. When applying the 5 km x 5 km deposition data for these purposes, important features of the landscape which occur at finer scales are not resolved, explicitly leading to uncertainty in exceedance estimates. Thus there has been pressure to resolve finer detail in the concentration and deposition fields, where possible from the monitoring data, to maintain a close link between the measurement networks and measures of the risk of damage.

As a part of the process in downscaling the deposition estimates, a set of maps at 1 km x 1 km resolution for the UK has been produced. Examples for wet-deposited NH_4^+ and NO_3^- are provided in Figure 3.27 to illustrate the main features of the high resolution maps.

The underlying concentration fields for ionic composition of precipitation are still based on 35 monitoring stations, and the ambient concentrations of the key gases (SO_2, NO_2, HNO_3 and NH_3, and their associated aerosol phase components) are provided by networks again of between 30 and 40 sites. The combination of modelling and interpolation needed to derive the 1 km x 1 km estimates utilise topographic and meteorological data in the downscaling. While the process understanding for both wet and dry deposition is adequate for the models, there are important uncertainties. In particular, the concentrations of reactive gases vary spatially due to complexity in the landscape (e.g. topography, local sources of the pollutants, the presence of woodland or isolated trees, etc.), and these effects are not captured by the relatively sparse monitoring sites. Thus, while the estimates are as far as possible unbiased on average, the values provided may differ from actual deposition at a specific location by a factor of two or more. Thus the application of the highly spatially resolved data will not necessarily yield better estimates of input to specific sites than the lower resolution data. The relatively small number of rural measurement sites used in the mapping is an important contributor to the uncertainty in deposition estimates. The uncertainty in site-specific deposition estimates is appreciably reduced if site-specific measurements of concentrations and the driving

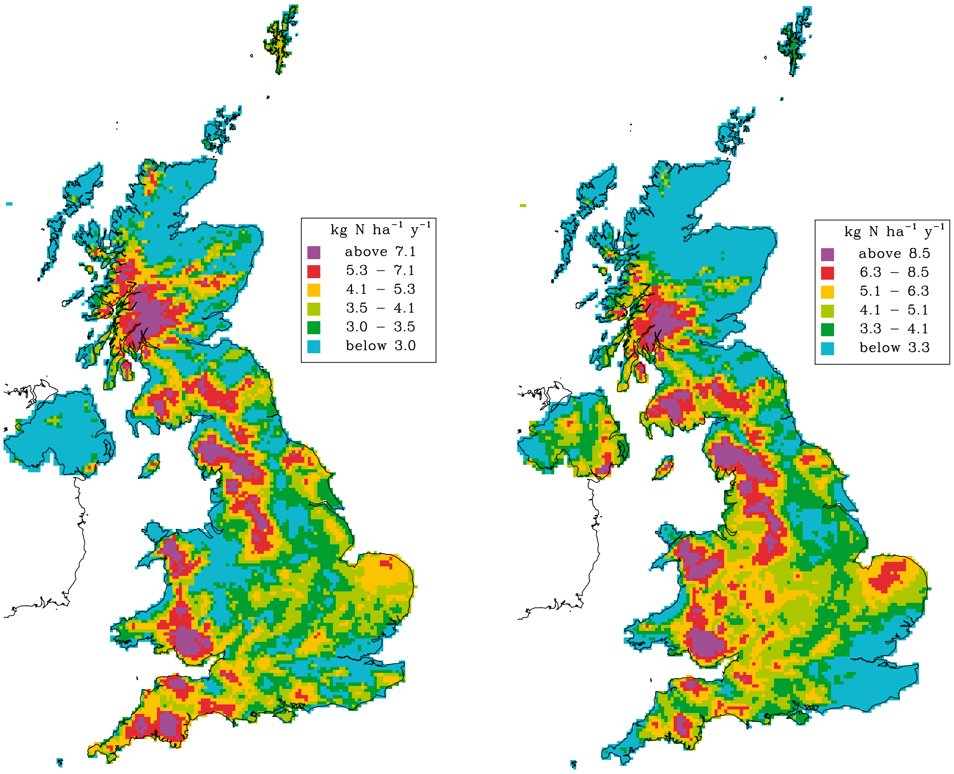


Figure 3.27 High resolution (1 km x 1 km) wet deposition maps for (a) NO_3^- and (b) NH_4^+ in the UK in 2005. Figure compiled using deposition data from UKEAP (2010).

meteorological variables are made. The measurements required are: concentrations of gaseous NH_3, NO_2 and HNO_3 in air, and NH_4^+ and NO_3^- in precipitation. To maximise the value of applications, potential users of the data are encouraged to consult the Centre for Ecology and Hydrology (CEH) team responsible for the maps (Ron Smith, ris@ceh.ac.uk, or David Fowler, dfo@ceh.ac.uk).

3.9 Ozone

The subject of ground level ozone (O_3) in the UK has recently been reviewed in AQEG (2009), which covers spatial and temporal patterns in ground level concentrations and the wider context of hemispheric background concentrations. Also included are trends in precursor emissions in the UK and more widely across Europe. The Royal Society has also reported recently on ground level ozone (Royal Society, 2008). This report draws attention to relevant policy issues and especially the necessary geographical scale for effective control of ground level ozone, which has been shown to be a hemispheric-scale environmental issue. Thus, regional or country-scale control measures have limited ability to regulate ground level ozone exposures within the control regions. These reviews will not be revisited here, but there are aspects of the subject of ground level ozone which are not covered in either of these reports and which are important in the overall RoTAP synthesis. The particular issues considered in this report are recent changes in the exposure of terrestrial ecosystems to ozone in the UK, both as long-term trends and changes in seasonal exposure. The effects of ozone on vegetation and human health have until recently been the main motivation for research and monitoring of ground level ozone. While these two effects remain the main policy drivers, the role of ozone as a contributor to the direct radiative forcing of global climate has grown in importance (IPCC, 2007). In addition, the recent recognition that the effects of O_3 on carbon sequestration through its effects on primary productivity of vegetation is emerging as an additional reason for interest in ground level ozone (Sitch *et al.*, 2007) and the effects on vegetation are the primary focus of RoTAP interest in ground level ozone.

The focus in earlier analyses of ground level ozone was on the peak O_3 concentrations which occur under warm, sunny conditions, and thus largely occur in the UK from April to September. Policy actions to date across Europe have reduced the emissions of NO_x and volatile organic compounds (VOCs) (ozone precursors) as reported in Chapter 2. These emission controls have reduced peak ozone concentrations by typically 30 ppb in the UK, but over the last 20 years mean concentrations have been increasing in urban areas due to reductions in local depletion of O_3 by NO, and in rural areas due to increases in the hemispheric background O_3 concentration. For the UK, the upward trends in the lower percentiles of the O_3 frequency distribution are clear at remote rural sites (Figure 3.28). Background concentrations of O_3 have increased by approximately 0.2 ppb per year, or by about 4 ppb over the last 20 years, and over much of rural UK this has led to the annual mean O_3 concentration increasing (see Figure 7.10 for the trend at Mace Head in the west of Ireland). The cause of the increases in background O_3 are increases in precursor emissions throughout the northern hemisphere, including shipping, aircraft, vehicle and industrial emissions in developing economies.

The trends in mean O_3 concentration bring current ambient values into the range in which effects on vegetation may occur and are therefore of interest in the effects assessment (Chapter 5). Given the trend in background O_3 in the UK, and the fact that in hot, dry summers, such as 2003, when ground level O_3 concentrations still reach 120 ppb

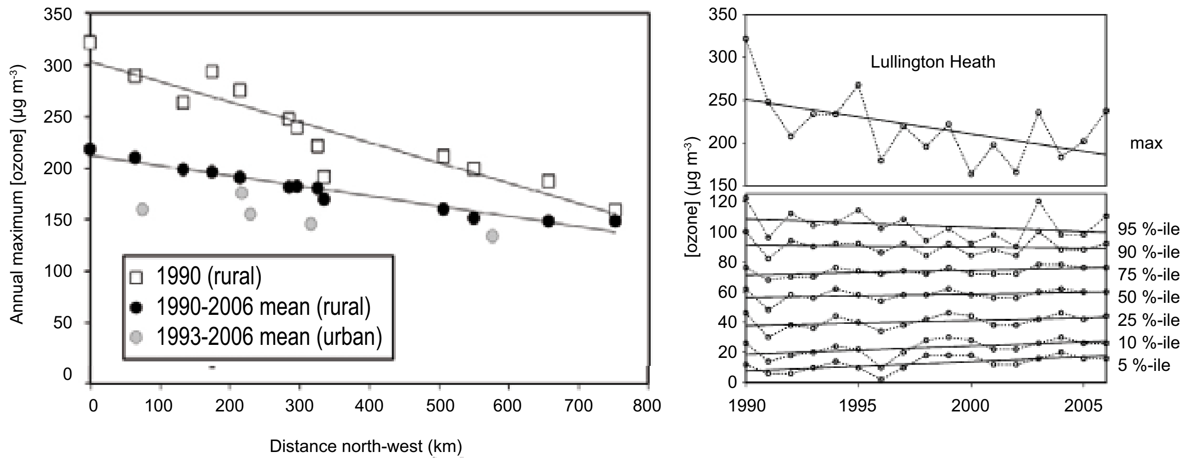


Figure 3.28: Trends in rural ground level ozone concentration throughout the UK between 1987 and 2006 (Adapted from Jenkin *et al.* (2008)).

widely, there remains a very serious threat of effects of O_3 on both crops and semi-natural vegetation throughout the UK.

The increases in background ozone concentrations and decreases in peak values shown in Figure 3.28 are common to rural areas throughout the UK and therefore are potentially important for effects on sensitive vegetation across the country. An important consequence of the changes in ozone climatology is that the main focus of interest is now on the mean and background contributions to ozone concentrations rather than on the peak values, as this exposure provides the majority of the threat to ecosystems as discussed in Chapter 5.

The data in Figure 3.29 show both the decrease in peak summer ozone occurrence and an increase in spring values. In particular, March AOT40 values are much larger in recent years than in the 1980s.

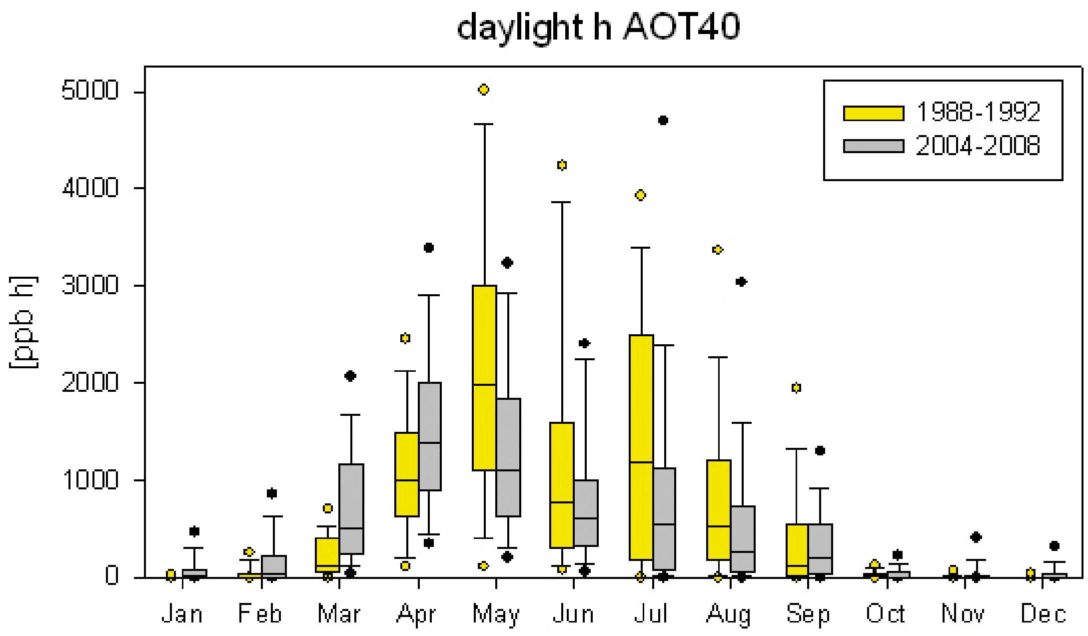


Figure 3.29: The seasonal occurrences of ozone above 40 ppb (quantified as AOT40) in 2004-08 compared with 1988-92 for rural sites in the UK. Data taken from the Air Quality Archive.

Spring and winter ozone concentrations in rural areas of the UK have increased steadily since the monitoring network was established in 1986. Larger concentrations have been observed from October through the winter until April in recent years, with potentially damaging ozone concentrations now occurring in all months of the year.

Winter peak values are consistently larger than they were 20 years ago. To illustrate the change in ozone exposure, Figure 3.30 shows a 36% increase in the number of hours in which ambient concentration exceeds 40 ppb and a reduction of 50% in the exceedances of 60 ppb over the ~20-year period. The cross-over point between concentrations that

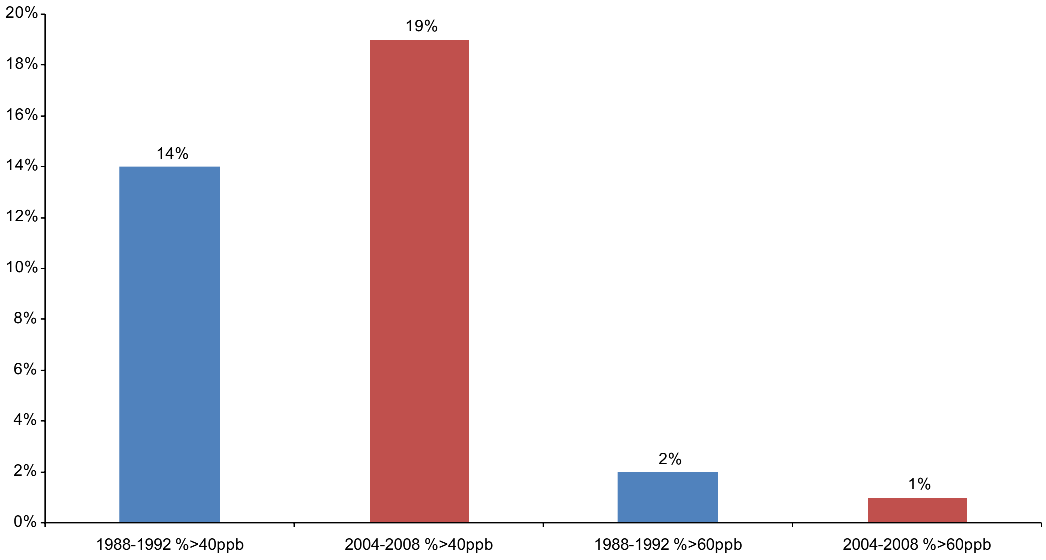


Figure 3.30: The percentage change in exceedances of 40 ppb and 60 ppb at 11 rural sites with data for all years in each 5-year period 1988-92 and 2004-08. Data taken from the Air Quality Archive.

are increasing in frequency of occurrence and those that are decreasing in rural areas is between 40 and 60 ppb in this dataset. The ecological effects of the changes in ozone exposure are discussed in Chapter 5.

The recent trends in peak values for ground level ozone reflect changes in emissions of ozone precursors (NO_x and VOCs) in the UK and Europe and are an important effect of the policies of emission reductions. However, the changes in background ozone in the UK are driven by emissions over the northern hemisphere, and well beyond the limited influence of control strategies in the UK or more widely in Europe, as detailed in Royal Society (2008).

3.10 Effects of changes in climate on atmospheric processing and deposition of air pollutants in the UK

The atmospheric processing of the pollutants considered in this chapter is sensitive to changes in the chemistry, dispersion and removal processes which are all coupled to climate (Isaksen *et al.*, 2009; Monks *et al.*, 2009). The period of the measurements on which the chapter is based, at 20 years, is short relative to the magnitude of changes observed in the driving variables (IPCC, 2007). This period is too short to seek direct evidence of an effect of climate on pollutant deposition in the UK. However, some distinct features in the inter-year variability are clear and these provide important clues to the kinds of changes we should expect as climate changes. The warm, dry summer of 2003 led to substantially reduced wet deposition (-30%) of most pollutants in the UK relative to adjacent years with approximately normal rainfall. Also in 2003, ambient HNO_3

concentrations were larger, by between 30% and 40%, and episodes of ground level O_3 concentrations were more frequent and larger in terms of peak concentration than in any other recent year, due to the prolonged warm weather and anticyclonic conditions which advected pollutants from continental Europe over the UK. The ozone episodes in 2003 exceeded 100 ppb over substantial areas of the UK and similar episodes in continental Europe were associated with a substantial increase in human mortality (Fischer *et al.*, 2004; Lee *et al.*, 2006).

3.11 Base cations

Base cation deposition in the UK has been monitored in wet deposition, as the main deposition pathway in most of the UK, from 1986 to the present, although there are some years in the early 1990s during which the data were not adequate for UK maps of deposition to be generated. The data have been used to calculate both wet and dry deposition, and this shows that wet deposition provides typically 80% of the total deposition and that the total deposition of base cations has declined by approximately 30% between 1986 and 2008.

Chapter 4 Modelling the Concentrations and Deposition of Pollutants over the UK

Summary

- Atmospheric Transport Models (ATMs) are powerful tools which provide estimates of the spatial distribution of concentrations and deposition of pollutants. They can be applied to estimating past and future trends as well as the attribution of emissions sources to pollutants.
- Accurate modelling of pollutant deposition and concentration requires appropriate parameterisation of meteorological, physical and chemical processes in the atmosphere and detailed mapping of pollutant emissions.
- Simple models have been applied to estimate trends and uncertainty in sulphur and nitrogen deposition in the UK. The preliminary results from complex models are available. Their further application is currently under development.
- The deposition of sulphur, oxidised nitrogen and reduced nitrogen in the UK is predicted to decrease between 2005 and 2020 by 47%, 32% and 16% respectively. Reduced nitrogen deposition will become relatively more important compared to oxidised nitrogen and sulphur deposition. Policy to further reduce nitrogen deposition and acid deposition will need to focus on control of emissions of ammonia.
- International shipping emissions contributed 18% and 19% respectively of the deposition of oxidised nitrogen and sulphur in the UK during 2005. With the implementation of the MARPOL Convention on emissions from international shipping, sulphur deposition from shipping will decline through the coming decade. Nitrogen oxides (NO_x) emissions from shipping will continue to contribute over 30% of total oxidised nitrogen (NO_y) deposition.
- Models are able to simulate peak ozone concentrations, such as those measured during the 2003 heatwave. However this requires accurate simulation of both local and meso-scale meteorology.
- There has been a significant decline from 1990 to 2005 in episodic peak ozone concentrations at central England locations, accounted for by European NO_x and volatile organic compound (VOC) emission reductions. Inter-year variability in intercontinental transport has overwhelmed the slight downwards trend that would be expected in annual mean ozone concentrations at these same locations from NO_x and VOC emission reductions.
- Future UK modelling should focus on the derivation of the ozone flux metric POD_Y, which can be linked quantitatively to effects on crops, forests and grasslands. There is a need to include validated algorithms for the calculation of POD_Y into UK ozone policy models.

4.1 Introduction

Modelling the concentration and deposition of air pollutants extends our knowledge of these compounds and their behaviour and provides an important addition to information obtained from measurement and monitoring programmes. In particular, models have the following advantages:

- Estimation of concentration and deposition at a large number of modelled grid cells provides more detailed spatial coverage than is generally possible with a monitoring network.
- Calculation of the fate of pollutants in the atmosphere and quantitative attribution of pollutant concentrations and deposition to their emissions sources.
- Assessment of past and future environmental change based on use of historical and projected pollutant emissions scenarios.

Modelling the emissions, transport, chemical transformation and deposition of atmospheric pollutants requires accurate numerical parameterisation of the underlying chemical, physical and meteorological processes. The degree of complexity involved in such parameterisations varies according to the type of model and the nature of the pollutant and process to be studied. The scale of models varies from local dispersion models to national, continental and global-scale models. In this chapter the focus is primarily on national-scale modelling. The properties of the models applied here to estimate concentrations of surface ozone and deposition of nitrogen and sulphur in the UK are summarised in the table in Appendix B.

Atmospheric Transport Models (ATMs) can be broadly grouped into two types: Lagrangian and Eulerian. In an Eulerian framework, the calculation of physical and chemical variables is undertaken simultaneously for all the grid points in the model domain. With a Lagrangian approach, calculations are made along a predefined trajectory which a parcel of air is assumed to follow. Large numbers of trajectories (typically tens of thousands) are required to generate statistically significant results. A major difference between the Eulerian and the Lagrangian approach is that whilst calculations in Lagrangian trajectories are independent, calculations at the grid locations of an Eulerian model are interdependent.

A further broad distinction between types of model is ‘simple’ and ‘complex’. Examples of simple models include FRAME, HARM (Metcalfe *et al.*, 2001) and TRACK (Lee *et al.*, 2000). These models use relatively simple chemical schemes, assume straight-line trajectories and are driven by annually averaged statistical meteorology (annual average precipitation map, wind frequency and wind speed roses). Their main advantage is a fast simulation time which allows them to be applied to source–receptor calculations (involving hundreds of model simulations (Oxley *et al.*, 2003; Vieno *et al.*, 2010a)) and uncertainty analyses (involving thousands of model simulations (Page *et al.*, 2008)), as well as use with finer grid resolutions covering extensive domains (Hallsworth *et al.*, 2010). Examples of complex Eulerian models include EMEP4UK and CMAQ. These models include more complex chemical schemes and require a detailed meteorological driver to simulate the temporal evolution of temperature, wind, humidity, cloud and precipitation in the atmosphere. The Photochemical Trajectory Model (PTM) (Derwent *et al.*, 2006; Derwent *et al.*, 2008) and the

Ozone Source-Receptor Model (OSRM) (Hayman *et al.*, 2006a; Hayman *et al.*, 2006b) are examples of complex Lagrangian models (employing detailed chemical schemes and driven by curved trajectories generated from a meteorological model). Such models are able to simulate short-term pollution events, the episodic nature of wet deposition of pollutants and the detailed interaction between pollutants and meteorology. A major development during recent years has been the move towards open access code for both atmospheric transport models and meteorological models. The result of these changes, combined with advances in computer technology, is that complex models have become available to the general air pollution modelling research community and can be run using medium-sized high performance computing facilities.

4.2 Nitrogen and sulphur deposition

Maps of deposition of sulphur, oxidised nitrogen and reduced nitrogen calculated by FRAME for the emissions year 2005 are shown in Figure 4.1. Wet deposition is highest in the hill areas of the Pennines and Wales, due to a combination of heavy precipitation and orographically enhanced concentrations in precipitation due to the seeder-feeder effect. High deposition of reduced nitrogen and sulphur also occurs in the source regions due to the solubility of the emitted primary gases, sulphur dioxide (SO_2) and ammonia (NH_3). Dry deposition of sulphur is highest close to the source areas of northern England and Greater London, as well as near ports and coastal areas due to the influence of SO_2 emissions from international shipping. Dry deposition of oxidised nitrogen is closely correlated to road transport, and is highest near the large urban areas of Greater London, Birmingham, Manchester and the major motorways. Dry deposition of reduced nitrogen shows strong local-scale variability and is closely correlated to emissions from livestock, notably cattle emissions from western England. The modelled total deposition budgets to the United Kingdom for sulphur, oxidised nitrogen and reduced nitrogen are shown in Table 4.1 For all three species, total national deposition is dominated by the wet deposition component in precipitation, with oxidised nitrogen and reduced nitrogen making similar contributions to total nitrogen deposition.

Table 4.1: UK deposition budgets of sulphur and oxidised and reduced nitrogen using emissions estimates for the years 1970, 1990, 2005 and 2020 modelled with FRAME.

Year	SO_x wet (Gg-S)	NO_y wet (Gg-N)	NH_x wet (Gg-N)	SO_x dry (Gg-S)	NO_y dry (Gg-N)	NH_x dry (Gg-N)
1970	343	97	126	346	99	67
1990	240	101	122	184	83	71
2005	106	82	105	51	66	66
2020	64	62	86	27	39	57

Assessment of the accuracy of the model (FRAME) in estimating atmospheric concentrations and deposition rates of gaseous and particulate compounds of nitrogen and sulphur has been made by comparison with measurements. For this purpose, data from the

National Ammonia Monitoring Network and the National Nitric Acid Monitoring Network using monthly sampling from DELTA samplers (DEnuder for Long Term Analysis) (Sutton *et al.*, 2001) were employed, together with results from the rural SO_2 and nitrogen dioxide (NO_2) monitoring networks and the secondary acid precipitation monitoring network. All monitoring data were averaged over the three-year period 2004-2006 to smooth out interannual anomalies caused by changing patterns in circulation and precipitation. The model was also driven with precipitation and wind statistics averaged over the same three-year period. The results of a sample of these scatter plots are illustrated in Figure 4.2 for the primary emitted gases (SO_2, NO_2, NH_3), sulphate wet deposition, ammonium aerosol concentrations and nitric acid concentration. A summary of the correlation statistics is given in Table 4.1. In general the model is able to well reproduce the measured concentrations of SO_2 and NO_2. A good correlation is found with measurements of sulphate, nitrate and ammonium aerosol concentrations, though there is some overestimate of sulphate and nitrate aerosol concentrations. Modelled wet deposition also shows a reasonable correlation with measurements. A considerable scatter is apparent in the correlation with measurements of ammonia concentration. This is caused by the local-scale variability in ammonia concentrations on a scale unresolved by the model 5 km grid. There is also considerable uncertainty in the magnitude and mapping of ammonia emissions from certain livestock categories, as discussed in Chapter 2.

Improvements to national-scale modelling of dry deposition of reduced nitrogen will require the development of models with a higher horizontal resolution. A poor correlation and underestimation is also found with nitric acid concentrations. This secondary compound is reactive, soluble and readily deposited to vegetation and therefore presents a greater challenge to be well represented in atmospheric transport models.

Table 4.2: Parameters for the FRAME model based upon 2005 data (Linear regression $y_{(modelled)} = m * x_{(measured)} + c$; R^2 is the correlation coefficient and % is the percentage of modelled values greater than half and less than twice the measured value. It is considered an acceptable level of performance if % > 50%. n is the number of measurement data points).

	m	C	R^2	%	n
SO_2 concentration	1.18	+0.03	0.95	92	12
SO_4^{2-} concentration	1.36	-0.09	0.92	92	12
NO_2 concentration	1.15	-0.37	0.94	100	26
NO_3^- concentration	1.27	-0.14	0.96	92	12
NH_3 concentration	0.90	+0.87	0.49	57	94
NH_4^+ concentration	0.98	-0.04	0.97	92	12
HNO_3 concentration	0.54	+0.24	0.67	75	12
SO_4^{2-} wet deposition	1.07	+0.08	0.68	78	38
NO_3^- wet deposition	0.89	+0.11	0.68	81	38
NH_4^+ wet deposition	0.90	+0.17	0.70	76	38

Table 4.3: Comparison of UK deposition budgets of sulphur and oxidised and reduced nitrogen calculated with the FRAME, EMEP and CMAQ models using the measured–interpolated CBED data as a common reference.

Year	SO_x wet (Gg-S)	NO_y wet (Gg-N)	NH_x wet (Gg-N)	SO_x dry (Gg-S)	NO_y dry (Gg-N)	NH_x dry (Gg-N)
CBED 2004-06	112	98	121	30	87	62
FRAME 2005	106	82	105	51	66	66
EMEP 2005	71	56	71	65	49	67
EMEP4UK 2006	76	48	71	46	53	66
CBED 2003	93	77	87	52	149	73
CMAQ 2003	57	38	41	132	70	93

The EMEP model is run at a 50 km scale over Europe. Dry and wet deposition of reduced nitrogen is illustrated in Figure 4.3. The model gives a similar spatial distribution of total reduced nitrogen (NH_x) dry deposition to FRAME but does not capture the fine-scale resolution of deposition associated with local variation in ammonia emissions from livestock. The spatial distribution for wet deposition is quite different to FRAME. With FRAME, wet deposition is closely linked to the high rainfall areas, whereas with EMEP wet deposition is highest in areas nearer the emissions sources. These differences occur partly due to the enhanced washout coefficient for orographic precipitation which is incorporated in FRAME but not included in EMEP. Another difference is a constant drizzle approximation in FRAME, whereas precipitation in EMEP is explicitly process- based and can wash out material closer to its source during heavy precipitation. The UK deposition budgets for EMEP and for the other models included here are shown in Table 4.3. Dry deposition budgets are similar to those from FRAME but wet deposition budgets with EMEP are significantly lower than FRAME.

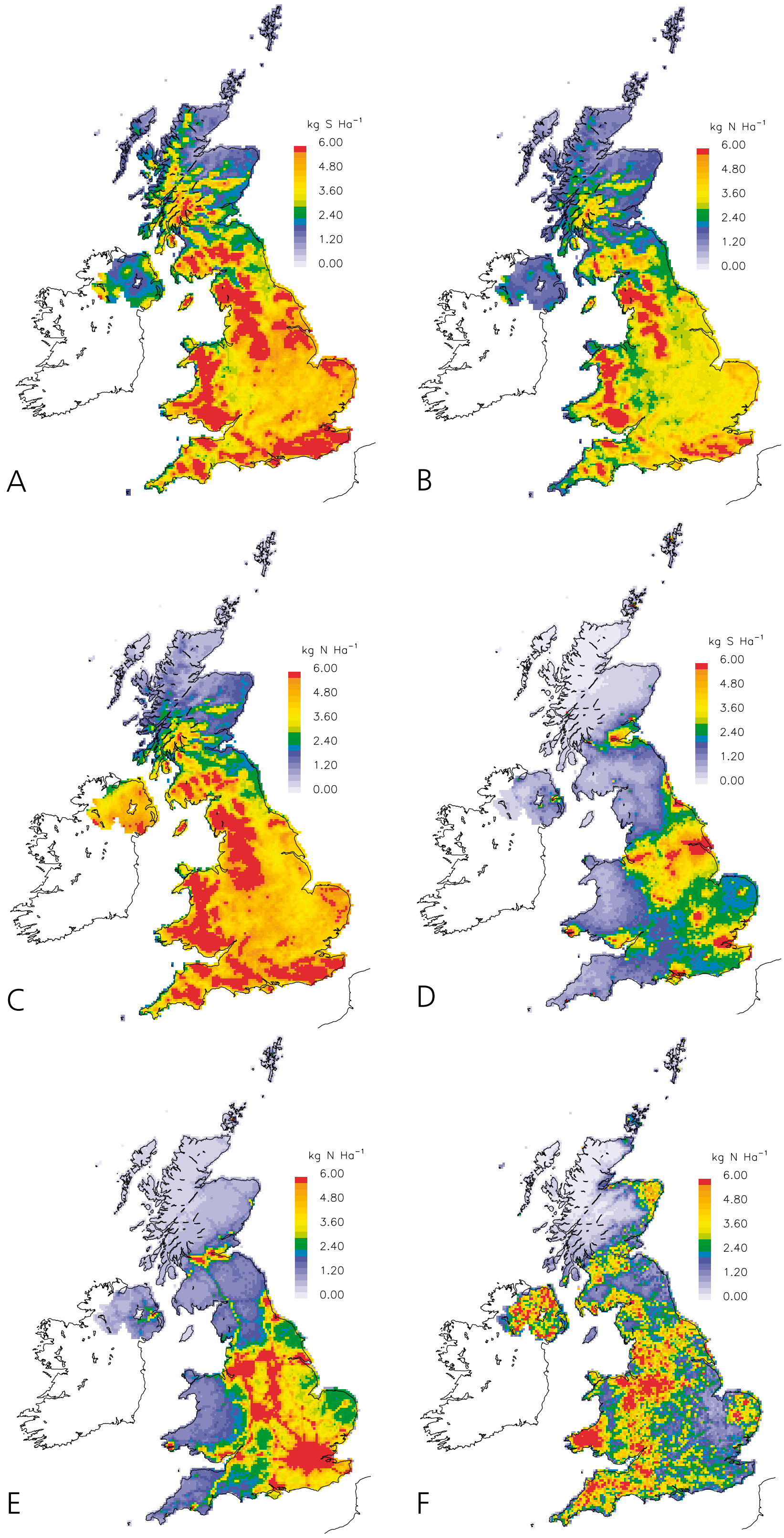


Figure 4.1: Deposition of sulphur and nitrogen modelled with FRAME for the year 2005 (kg N/S ha^{-1}): (a) total oxidised sulphur (SO_x) wet deposition, (b) total oxidised nitrogen (NO_y) wet deposition, (c) total reduced nitrogen (NH_x) wet deposition, (d) SO_x dry deposition, (e) NO_y dry deposition, (f) NH_x dry deposition.

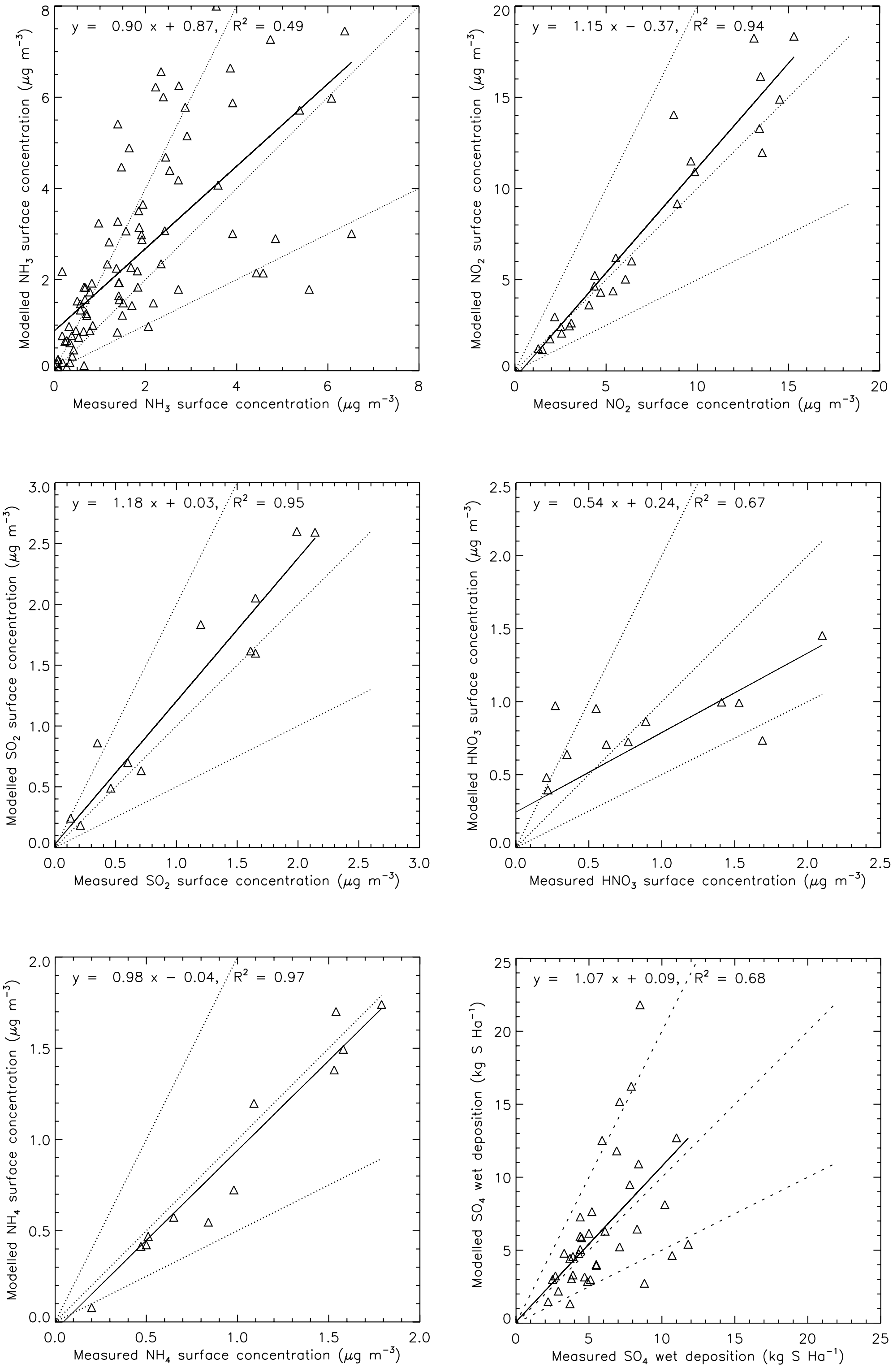


Figure 4.2: Correlation of the FRAME model for the year 2005 with measurements of NH_3 concentration (upper left); NO_2 concentration (upper right); SO_2 concentration (middle left); HNO_3 concentration (middle right); NH_4^+ aerosol concentration (lower left); SO_4^{2-} wet deposition (lower right). Measured data are taken from UKEAP (2010). (It is considered an acceptable level of performance if half the points on the scatter plots lie between the 0.5 to 1 and the 2.0 to 1 lines).

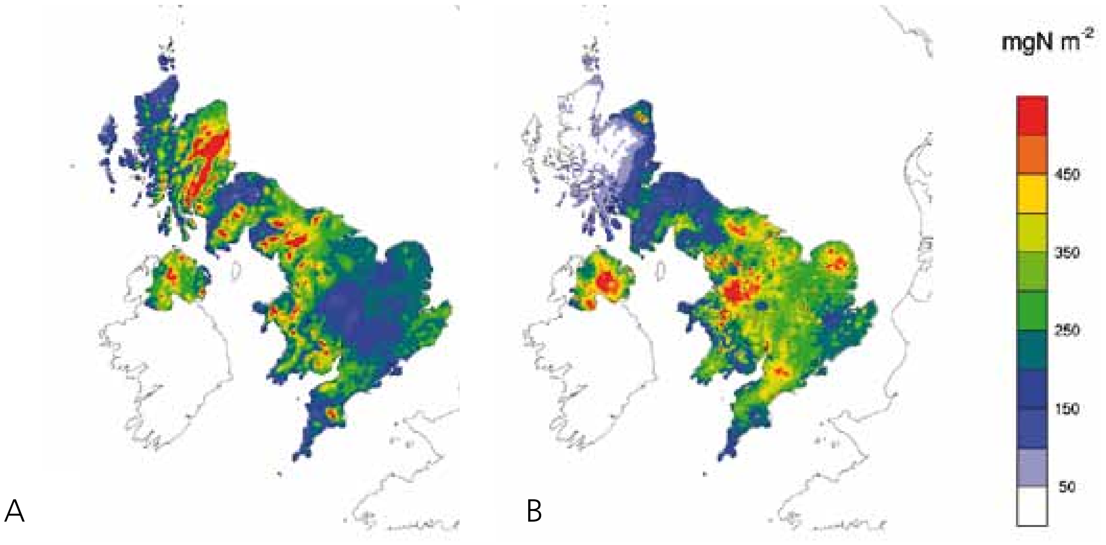


Figure 4.3: EMEP modelled (a) dry and (b) wet deposition of NH_x for the year 2005 (kg N ha^{-1} yr^{-1}).

Whilst measures have been introduced to reduce emissions of SO_2 and nitrogen oxides (NO_x) from the UK and other European countries, emissions from international shipping have not been subject to the same controls. The sulphur content of bunker fuel is estimated to be 2.7% on average and globally emissions from international shipping are thought to be growing at a rate of 2.5% per year (Endresen *et al.*, 2003). However, considerable uncertainty in both the magnitude and spatial distribution of shipping emissions remains. In most European waters, the spatial resolution of shipping emissions is currently 50 km, which is inadequate to accurately investigate deposition of sulphur and nitrogen in coastal areas. The influence of emissions of SO_2 from international shipping on sulphur deposition in the UK has been assessed with the FRAME model (Dore *et al.*, 2007). Due to heavy traffic of shipping in the English Channel and in port regions, dry deposition of SO_2 from shipping is highest in south-east England (Figure 4.4). An agreement has been made by the International Maritime Organization to globally reduce the sulphur content in bunker fuel to 0.5% by 2020, and to 0.1% in the North Sea and English Channel.

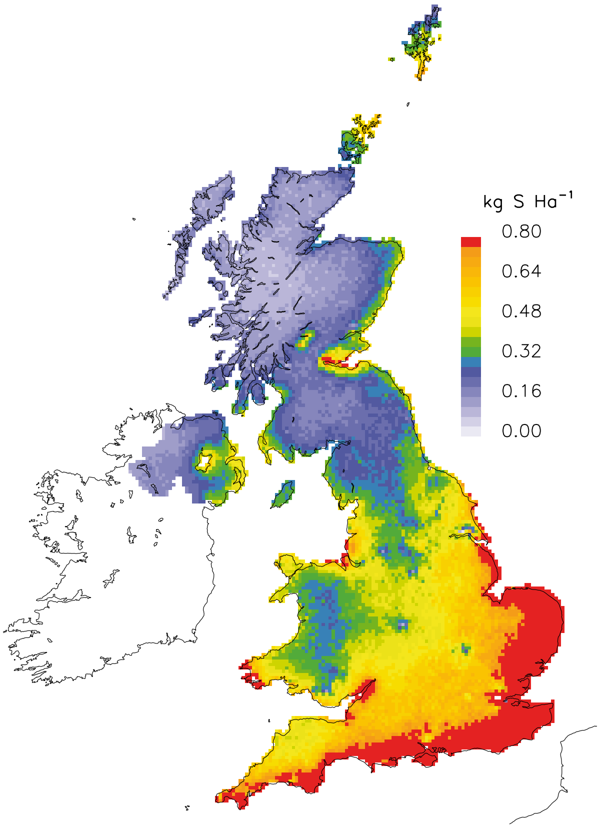


Figure 4.4: Contribution of international shipping to dry deposition of total oxidised sulphur (SO_x) modelled with FRAME for the year 2005 (kg S ha^{-1}).

Implementation of the agreement means that by 2020, sulphur dioxide emissions from shipping will no longer be a significant contribution to sulphur deposition in the UK. The contribution to total oxidised nitrogen (NO_y) deposition in the UK of NO_x emissions from international shipping is likely to remain high (at approximately 30% for 2020). Future studies will make use of higher resolution (5 km) emissions from international shipping in the coastal region of the UK.

Results from the EMEP4UK model for 2006 are shown in Figure 4.5a for reduced nitrogen dry deposition and Figure 4.5b for reduced nitrogen wet deposition. The model is able to capture the spatial variability of ammonia dry deposition when qualitatively compared with other studies such as Singles *et al.* (1998) and Dore *et al.* (2006; 2007). For wet deposition, the spatial pattern reproduces well the higher wet deposition over mountainous terrains as presented by Dore *et al.* (1992) and Fournier *et al.* (2005b). The present analysis shows that the key challenge is to be able to capture the spatial scale of orographic precipitation. Orographic features are not well resolved when the EMEP model is run with a 50 km x 50 km grid resolution. By contrast, using the scale of 5 km x 5 km in EMEP4UK, the main features of UK orography and their influence on air flow, cloud formation, precipitation and wet deposition are better resolved.

The CMAQ (Community Multiscale Air Quality) Eulerian modelling system version 4.6 was also run for the year 2003, using three nested grids with the inner grid covering the whole of the UK at a horizontal resolution of 5 km on 15 vertical levels. Meteorology

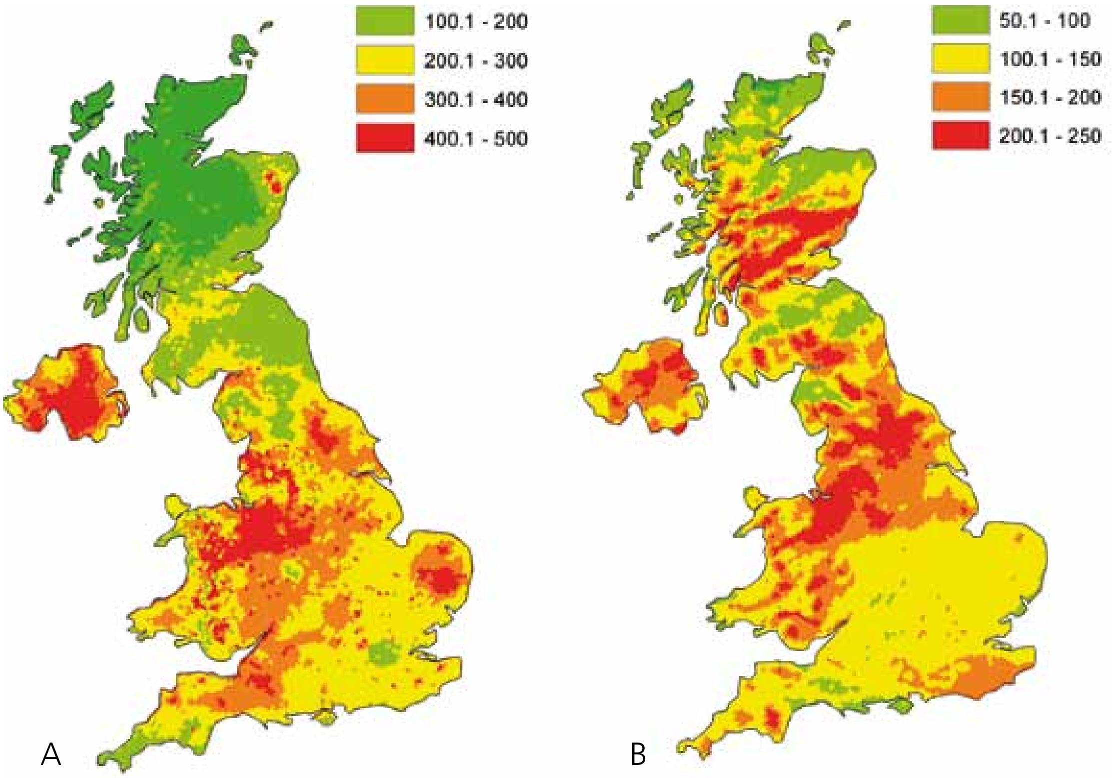


Figure 4.5: EMEP4UK calculated annual reduced nitrogen deposition for the year 2003, (a) dry deposition and (b) wet deposition (Units are mg N m^{-2} yr^{-1}; note different scales).

for the period was calculated using the Weather Research and Forecasting (WRF) model version 3.0.1.1, which was nudged towards ECMWF analyses every 6 hours. Emissions data from the National Atmospheric Emissions Inventory (NAEI) for the UK and from EMEP for grid cells outside of the UK were processed using the Sparse Matrix Operator Kernel Emissions (SMOKE) pre-processor version 2.4. The CMAQ simulations were set up using standard options for the representation of physical and chemical processes, including the CB05 gas phase chemistry mechanism and the AERO4 aerosol module which treats sea-salt aerosols.

Deposition of wet and dry non-sea-salt sulphur is illustrated in Figures 4.6a and 4.6b respectively. A strong west to east gradient in deposition is evident across the country, with wet deposition highest in the upland, high rainfall areas in the western part of the country. Dry deposition of sulphur is highest in the East Midlands and Greater London. A comparison of deposition budgets for CMAQ and the CBED (Concentration Based Estimated Deposition) measured–interpolated data for the year 2003 is illustrated in Table 4.3. It should be noted that 2003 was a year characterised by specific meteorology with high summer temperatures and the lowest annual precipitation of the last two decades. This resulted in lower than average wet deposition and relatively high dry deposition. A verification of the CMAQ model by comparison with monthly measurements of air concentrations of acidifying and eutrophying gases and particles is described in Chemel *et al.* (in press). Significant differences are apparent for the different models and the measured–interpolated data. The application of Eulerian models to sulphur and nitrogen deposition at a fine-scale resolution in the UK is currently in a state of development. These models offer the opportunity to represent deposition in a more physically realistic process-based way. Their further development and application is recommended. A comparison of complex models with measurements of precipitation and of wet deposition as well as gas concentrations (SO_2, NO_x, NH_3 and nitric acid (HNO_3)) and aerosol concentrations (sulphate, nitrate and ammonium) will be undertaken in the

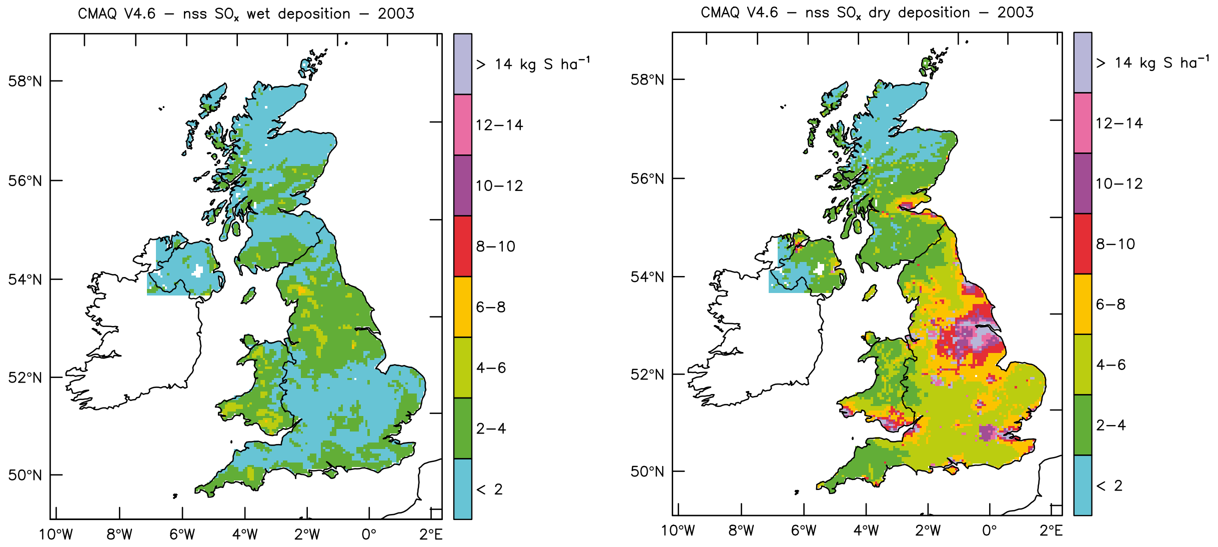


Figure 4.6: CMAQ calculated annual non-sea-salt sulphur deposition for the year 2003, (a) wet deposition and (b) dry deposition (kg S ha^{-1} yr^{-1}).

future. This will include comparison between the deposition generated by simple and complex models.

Complex models with detailed chemical schemes also provide an opportunity to study atmospheric processes. Simulations were conducted with CMAQ to consider the influence of abatement of gaseous emissions on particulate formulation. The biggest effect of the chemical interactions was found to be where a 30% reduction in NH_3 emissions implied a more than 30% reduction in fine particulate nitrate (NO_3) concentration, a greater change than when NO_x emissions were reduced by 30%. This suggests that in some regions of the UK, NH_3 may have a limiting effect on NO_3^- formation, due to the chemical equilibrium between gaseous NH_3 and HNO_3, and the ammonium nitrate ($NH_4^+NO_3^-$) aerosol.

Atmospheric transport models may be used to calculate past and future deposition of sulphur and nitrogen using historical estimates and future projections of gaseous emissions. For the UK, these estimates cover a 50-year time span from 1970 to 2020 (see Chapter 2). The FRAME model was run to calculate deposition of sulphur and of oxidised and reduced nitrogen for the years 1970, 1990, 2005 and 2020. The results of the deposition budgets for the UK are illustrated in Table 4.2. Reductions in wet deposition of total oxidised sulphur (SO_x) and nitrogen (NO_y) during the period 1990-2005 (56% and 19% respectively) were significantly lower than the changes in UK emissions during the same period (81% and 45% respectively). This occurred partly due to the fact that shipping emissions of SO_2 and NO_x did not decrease during this period and also that emitted gases were more rapidly oxidised to form sulphate and nitrate aerosol. Reductions in both wet and dry deposition of reduced nitrogen were small (14% and 7%) due to a lower reduction in emissions. The decrease in dry deposition of sulphur was lower than the decrease in emissions due to both the influence of shipping emissions and the increased deposition velocity of SO_2 to vegetation (Fowler *et al.*, 2007a). Significant further reductions in total deposition are forecast between 2005 and 2020 of 47%, 32% and 16% for SO_x, NO_y and NH_x respectively. A detailed study of modelled trends in deposition of sulphur and nitrogen, including comparison with the historic series of wet deposition is included in Matejko *et al.* (2009). The more modest decrease in reduced nitrogen deposition shows that ammonia will become, relative to oxidised nitrogen and sulphur, a more important pollutant in the future. Accurate high resolution emissions estimates and modelling at a national scale will be required to assess the contribution of reduced nitrogen to eutrophication. Hallsworth *et al.* (2010) showed that the area of Special Areas of Conservation (SACs) and Special Protection Areas (SPAs) exceeding critical levels for ammonia of 1 mg m^{-3} and 3 mg m^{-3} (for lichens and bryophytes and for higher plants respectively) was significantly reduced by increasing model resolution from 5 km to 1 km, due to more accurate mapping of emissions.

4.3 Surface ozone

Ozone (O_3) is a relatively strong oxidising agent which, in sufficient concentrations, can be detrimental to human health, inhibit the growth of crops and damage natural ecosystems. Under various international agreements and also UK legislation, the

Department for Environment, Food and Rural Affairs (Defra) is required both to monitor ozone together with other pollutants, and also to model its formation. Modelling ozone formation is required to assess the current UK situation and so try to ensure compliance with the prescribed exposure limits. Modelling is also needed to produce future scenarios to predict the likely effects of current and proposed air quality legislation in the light of expected economic growth and the consequent change in emissions. A detailed description of the different ozone models is contained in AQEG (2009).

4.3.1 Ozone Source–Receptor Model

The Ozone Source–Receptor Model (OSRM) is a boundary layer trajectory model. It is described in Hayman *et al.* (2010) and its key features are presented in the table in Appendix B. The OSRM calculates hourly concentrations for O_3, nitric oxide (NO) and nitrogen dioxide (NO_2) for a calendar year and, in principle, any O_3 (and NO_x) metric can be derived. In this section, the discussion will focus on concentration- and flux-based metrics related to the impacts on ecosystems. Modelling of ozone in urban areas using the OSRM will not be discussed as this was covered in the AQEG report on ozone (AQEG, 2009).

Figure 4.7 presents a scatter plot of modelled against measured annual mean concentrations of O_3, NO, NO_2, NO_x and O_x (= NO_2+O_3) for 41 UK monitoring sites in rural and urban background locations using year-specific emissions and meteorology for the years 1999 through to 2006. The O_3, NO_2 and O_x results lie close to the 1:1 line. There is more scatter in the results for NO (and hence NO_x). This indicates an acceptable level of model performance, especially in urban areas.

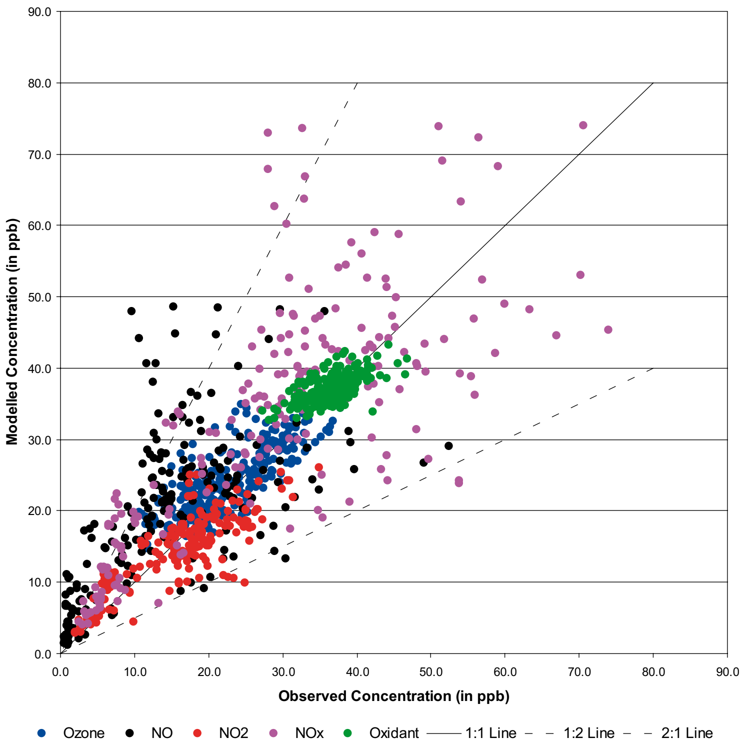


Figure 4.7: Scatter plot of the modelled (OSRM) against observed (AURN) annual mean mixing ratios of O_3 (blue), NO (black), NO_2 (red), NO_x (purple) and O_x (= O_3+NO_2, green) for 41 UK monitoring sites for the years 1999-2006.

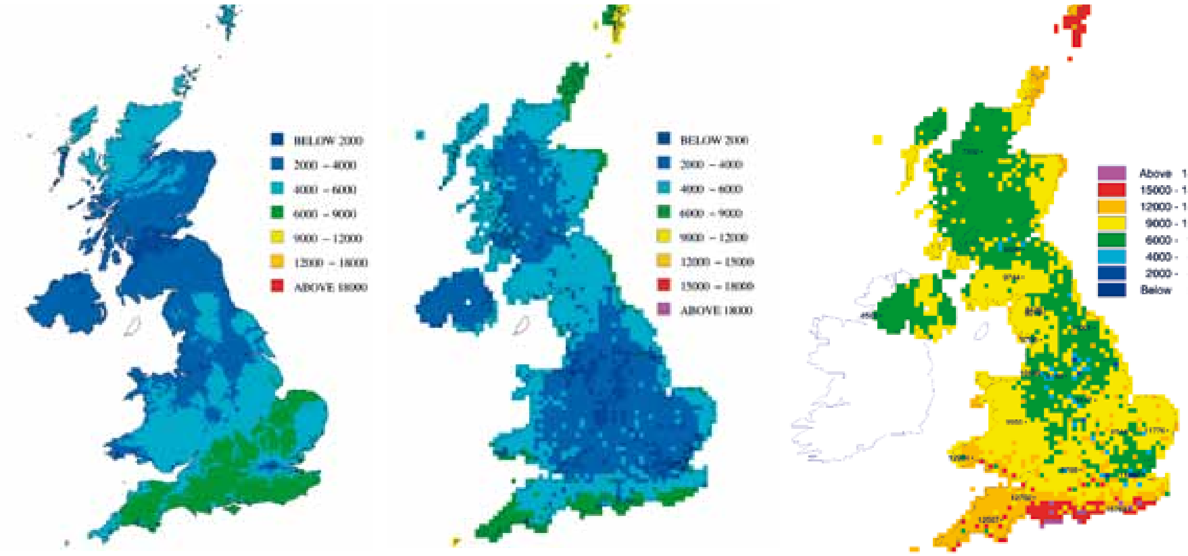


Figure 4.8: UK maps of the metric AOT40 (crops) (in µg m^{-3}.hours), as modelled using the empirically-based Pollution Climate Model (left-hand panel) and OSRM (middle panel) for the years 2000-04, and using OSRM for 2020 (right-hand panel).

Until recently, assessment of the risk of ozone impacts on vegetation was conducted using the AOT40 index. The left-hand panel of Figure 4.8 shows a UK map for the metric AOT40 (crops) for the time periods (May-July inclusive) specified in the 3rd Daughter Directive relating to ozone in ambient air (CEC, 2002). The map is derived from ozone measurements using the empirically-based Pollution Climate Model (PCM) (Murrells *et al.*, 2008); see also Stedman and Kent (2008) for the methodology) and is an average for the years 2000 to 2004. The middle panel shows the corresponding map derived using OSRM for a 10 km x 10 km grid covering the UK. As noted in previous comparisons (Hayman *et al.*, 2006a), the OSRM map shows broadly similar spatial patterns compared to the empirical maps, although there are some specific differences. The period includes the photochemically active year of 2003. As the OSRM was unable to capture the high concentrations in the southern half of the country during these episodes, the OSRM map gives lower values of the AOT40 metric. The right-hand panel shows the map for 2020 calculated by the OSRM for the base case scenario used for the Review of the Air Quality Strategy (Defra, 2007; Hayman *et al.*, 2006b). The increase in the AOT40 metric largely reflects the changes assumed in hemispheric ozone concentrations (based on the monthly trends for the scenario 'business as usual with climate change' in Derwent *et al.* (2006)). Without this change, the regional emission controls would have led to a slight reduction in the metric in rural areas.

Within the Convention on Long-range Transboundary Air Pollution (CLRTAP), flux-based metrics have been approved for use to assess the impact of ozone on vegetation (UNECE, 2004). Ten critical levels based on the flux-based POD_Y index (Phytotoxic Ozone Dose above a threshold of Y) have been recommended for use within CLRTAP; these are described in detail in Chapter 5. Since the POD_Y index is more appropriate than the AOT40 index for risk assessment in the UK, and since the POD_Y index gives a very different spatial distribution of risk across Europe (Simpson *et al.*, 2007), it is important to assess the ability of models to predict values of both AOT40 and POD$_Y$. The left-hand panel of Figure 4.9 compares the AOT40 (crops) metric calculated using OSRM for Harwell for the years 1999 to 2006 with those derived from the hourly O_3 measurements. The right-hand panel shows the accumulated ozone fluxes (POD$_Y$) over the threshold for winter wheat and for potatoes, as derived for Harwell from the observed and modelled hourly concentrations.

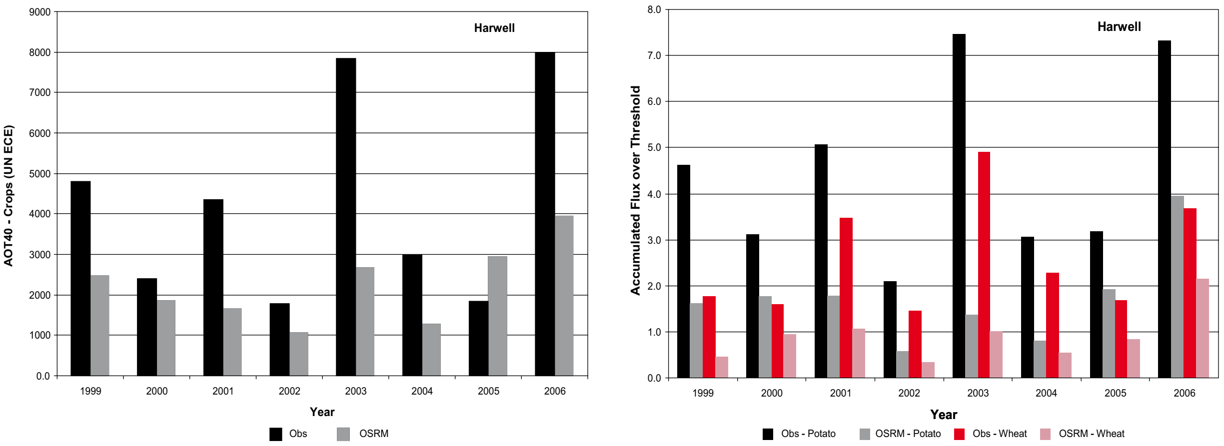


Figure 4.9: Observed (AURN) and modelled (OSRM) AOT40 (crops) (in ppb.hours, left-hand panel) and PODY (in mmol m^{-2}) for wheat (black) and potato (red) as derived from the measured hourly ozone concentrations (solid bars) and as calculated using the OSRM (hashed bars) for Harwell for the years 1999-2006.

The value of POD$_Y$ is generally underestimated at this site. 2003 and 2006 were photochemically active years with a number of significant photochemical episodes. Analysis of the 2003 episodes by Solberg *et al.* (2005) has indicated that emissions from forest fires contributed to the high O_3 concentrations and these emission sources were not included in the OSRM. Further, the OSRM assumes that the loss of ozone through stomatal uptake is always occurring (according to prescribed seasonal and diurnal patterns), even under meteorological conditions when the stomatal conductance is likely to be low. This results in a higher loss of ozone through deposition and may contribute to the underestimation of the metrics in 2003 and 2006. Finally, as discussed by Sofiev and Tuovinen (2001), small changes or biases in the modelled ozone concentrations close to the cut-off concentration can cause a significant change in both the AOT40 and POD$_Y$ metrics. Model performance at the other sites used varied from underestimation through reasonable agreement to overestimation of the modelled metrics when compared to observed values.

Using the then current base case emission projections for 2020, the assumption made on the future trend in hemispheric ozone concentrations led to a significant increase in modelled ozone concentrations and hence in concentration- and flux-based metrics across the UK. As noted by the Air Quality Expert Group (AQEG, 2009), both the strength and the sign of the trend in hemispheric ozone are however uncertain. Corresponding model runs in which there was no increase in hemispheric ozone concentrations led to a reduction in concentration- and flux-based metrics outside of urban areas, a result of the controls on ozone precursor emissions expected across the UK and Europe.

As will be explained in Chapter 5, although AOT40-based critical levels have been retained for use within CLRTAP, the use of AOT40 to assess the size of any effect of ozone on crop yields, forest growth or other response variables is flawed. Only the POD_Y index is recommended for assessing the size and extent of ozone impacts, and hence for quantification of the benefits of policy measures. It is therefore recommended that the derivation of ozone flux metrics, and specifically the POD_Y index, should be a routine output of ozone policy models in the UK.

There are considerable methodological and observational difficulties inherent in the modelling of the stomatal fluxes to vegetation across the UK and Europe. The European-scale EMEP model, which has been used in the assessments presented in Chapter 5, incorporates the DO3SE model (Emberson *et al.*, 2001) of ozone flux and deposition, which has been extensively tested against measured ozone fluxes to crops, forests and semi-natural ecosystems. There is a need to incorporate the algorithms of the DO3SE model that have been extensively tested and incorporated into the EMEP model, into UK-scale ozone policy models.

4.3.2 EMEP4UK

The EMEP4UK model was used to calculate ozone surface concentrations for 2003 with a horizontal resolution of 5 km × 5 km (Vieno *et al.*, 2010b). The model generally agrees well with observations for most of the sites of the Automatic Urban and Rural Network (AURN) though performance is limited against the specific TORCH campaign observations during 2003 as explained below. Figure 4.10 shows an example of the hourly time series comparison of EMEP4UK surface ozone versus AURN observation for Aston Hill. The model is able to capture ozone peaks in summer when strong photochemistry activity is more likely, and the lower values and less daily variability of ozone in winter/autumn when the background level of ozone is more important.

Hourly surface ozone was calculated for August 2003 using the EMEP4UK model and results are presented for Writtle during the Tropospheric ORganic CHemistry experiment (TORCH) and for Wicken Fen (East Anglia, England, a rural site). Figure 4.10 shows a comparison with observation from the AURN (Wicken Fen) and Writtle (TORCH). The hourly EMEP4UK model-predicted ozone surface concentrations for August 2003 agree well with observations at Wicken Fen.

The EMEP4UK model is also able to represent ozone at the TORCH campaign site (Writtle) as shown in Figure 4.10. However, for the 2nd, 3rd, 9th and 11th of August 2003 the model somewhat underestimated the measured surface ozone concentration. This appears to be related to the EMEP4UK model simulated surface NO_2 concentrations. NO_2 is overestimated by the EMEP4UK model at this location for the 2nd, 3rd and 9th of August 2003. This overestimation of NO_2 is probably the cause of underestimation of ozone on these days. The model 5 km × 5km grid square may not always be representative of the TORCH site. Interestingly, the model performs much better on these days at the Wicken Fen site which is only approximately 60 km away from Writtle, suggesting that local factors are causing the model–observation discrepancies.

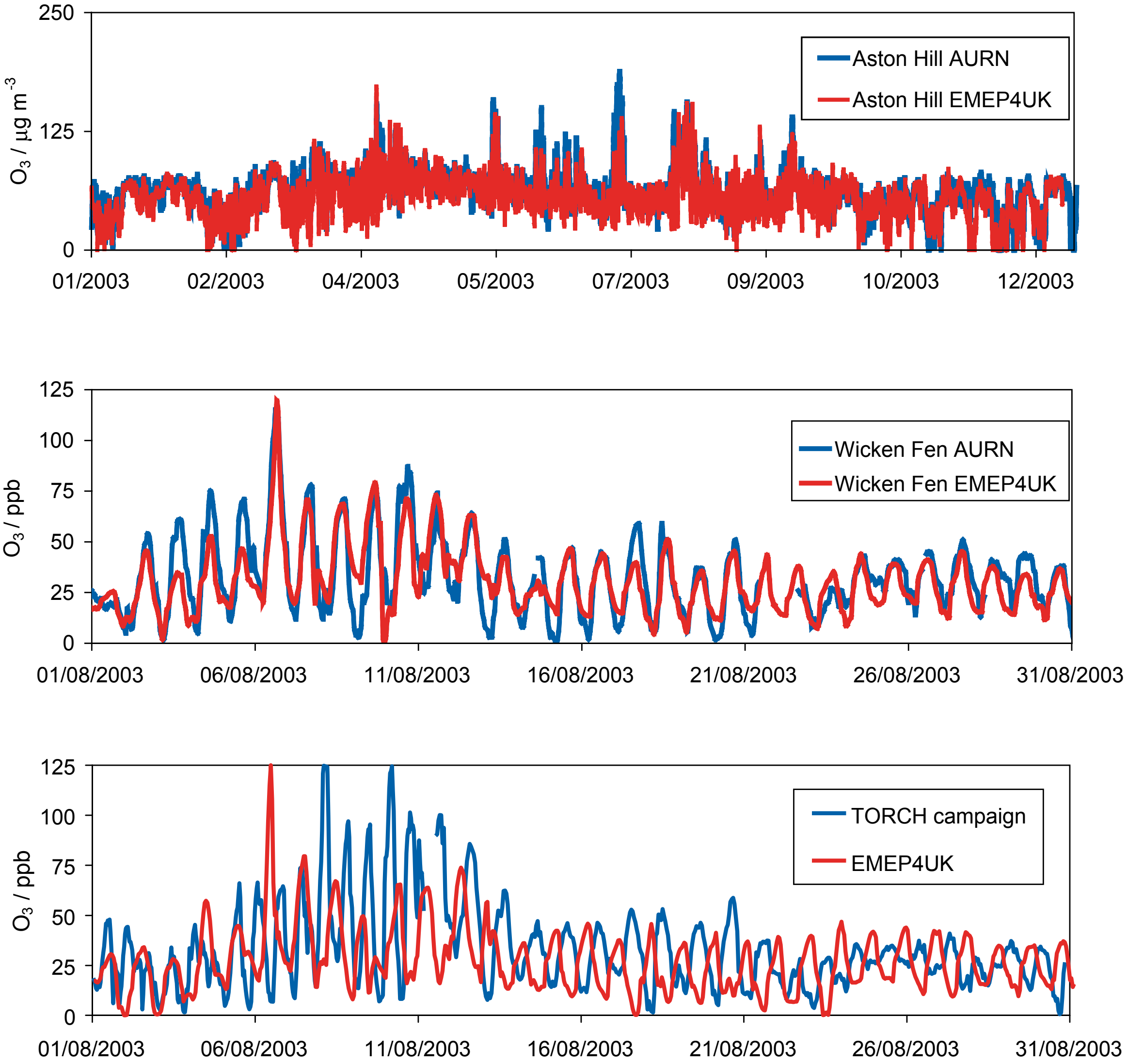


Figure 4.10: Hourly time series of EMEP4UK modelled (red) and measured (blue) surface ozone during 2003 at Aston Hill (AURN, upper), Wicken Fen (AURN, middle) and Writtle (TORCH, lower).

Six sensitivity experiments were carried out with EMEP4UK with the aim of investigating the nature of the ozone peaks at the Writtle site and these are summarised in Figure 4.11. The response of ozone to isoprene emissions appears to be approximately linear, with a doubling of emissions having roughly the opposite effect of switching the emissions off completely. Isoprene emissions contribute up to ~10 ppb ozone on some days. When compared with observations, the EMEP4UK model predicted isoprene in better agreement with double isoprene emissions (not shown here). Halving anthropogenic non-methane volatile organic compound (NMVOC) emissions decreases surface ozone by as much as ~15 ppb, whereas with a 50% increase the response is to increase ozone by up to ~30 ppb.

Surface ozone concentration is strongly affected by NO_x emissions and dry deposition. Halving NO_x emissions enhanced surface ozone by up to ~70 ppb on one day during the heatwave (9th August), whilst on other days it had little impact. Since 9th August also represented one of the key periods of O_3 discrepancy, this sensitivity test further supports the conclusion (noted above) that the deviations were particularly related to uncertainties in local patterns of NO_x emission. When NO_x emissions are reduced, NO_x does not accumulate as fast during night-time and late afternoon and therefore ozone production is not limited or depleted so fast by direct reaction of ozone with nitric oxide (NO) (titration).

Dry deposition also strongly controls surface ozone. Ozone dry deposition shows a large diurnal cycle because the stomata deposition is a strong function of temperature. Surface ozone is increased by up to 50 ppb when dry deposition is switched off completely. The higher effect is at night-time (~50 ppb) whereas in daytime the increase is ~30 ppb.

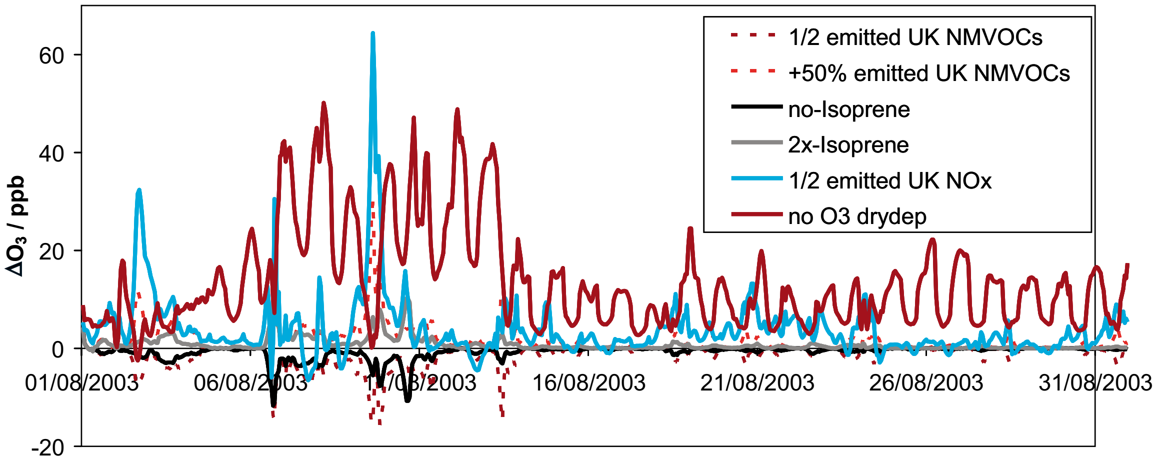


Figure 4.11: Enhancement of ozone surface concentration for different sensitivity experiments referred to a base run of the EMEP4UK model for August 2003 at Writtle (TORCH) site.

4.3.3 UK PTM: Modelling ozone trends, 1990-2010

The UK Photochemical Trajectory Model (PTM) has been set up to study both episodic peak and annual mean ozone metrics using UK and European NO_x and VOC precursor emissions for the years 1990, 1993, 1996, 1999, 2002 and 2005. The calculations were initialised using the observed baseline ozone levels for each year taken from the Mace Head historical record to simulate the year-by-year variations in intercontinental trans-Atlantic ozone transport. Studies of the episodic peak ozone metric have used constant meteorology based on that for the PUMA Campaign (Pollution of the Urban Midlands Atmosphere (Harrison *et al.*, 2006)) in 1999 centred on a location in the west Midlands at the University of Birmingham (Aston Hill). Studies of the the annual mean metric have used the daily meteorology for the full year 2005 based on a rural location in the south Midlands at Harwell, Oxfordshire. All meteorological data have been prepared by the Met Office using the NAME model. The aim has been to determine the contribution to the observed trends in the ozone metrics from:

- NO_x and VOC precursor emission reductions
- intercontinental trans-Atlantic ozone transport

- non-linearities in ozone formation
- the ambition level achieved in international policy negotiations.

Figure 4.12 illustrates the UK PTM results for episodic peak ozone over the period 1990-2010 using three different chemical mechanisms: MCMv3.1, MCM CRIv2.0 and CBM4. MCMv3.1 is a detailed chemical mechanism containing over 13,000 chemical reactions, MCM CRIv2.0 is of intermediate complexity with just under 1200 reactions and CBM4 is highly compact with about 100 chemical reactions (AQEG, 2009). There appear to be no significant differences between the year-by-year trends as a result of the choice of mechanism. The model appears to be able to reproduce well the observed trends in episodic peak ozone at the Harwell and Aston Hill locations using constant 1999 PUMA meteorology.

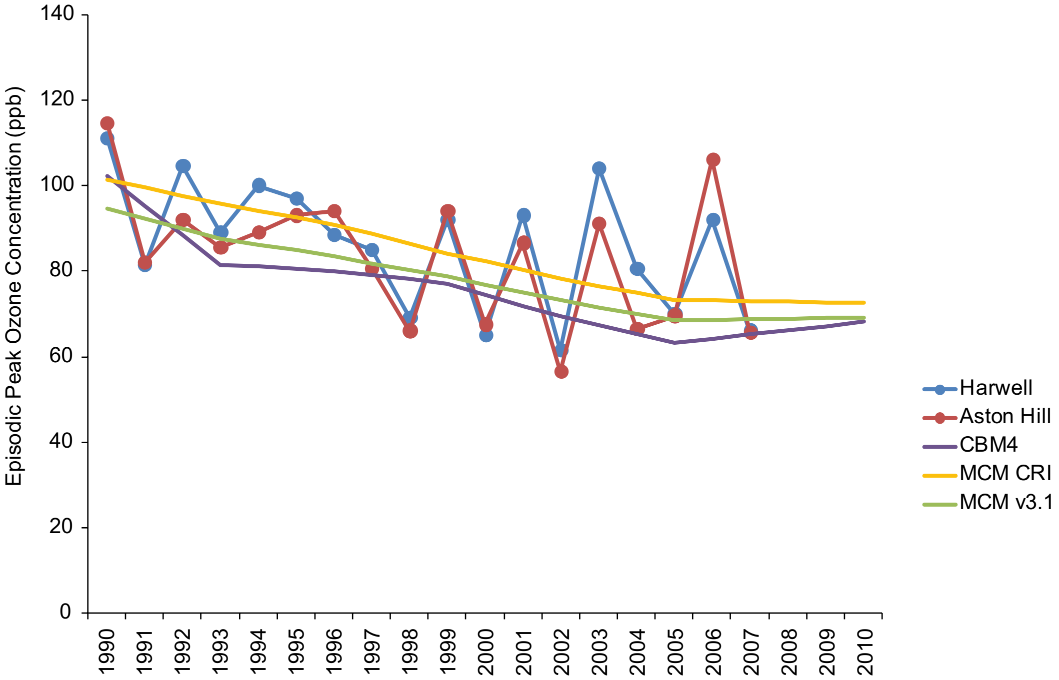


Figure 4.12: Observed (AURN) and modelled (PTM) trends from 1990 through to 2010 in episodic peak ozone for locations in the Midlands showing the influence of emission reductions.

This shows that there has been a strong influence of UK and European NO_x and VOC emission reductions on episodic peak ozone levels. Two years, however, stand out as exceptional, 2003 and 2006. These years have been strongly influenced by biomass burning in Portugal (Solberg *et al.*, 2008) and the Russian Federation (Witham and Manning, 2007). 2003 was also an unusually hot summer with generally high ozone concentrations across Europe.

By setting the model initialisations to the 2005 values and repeating the model calculations, a small decrease in the model trends was found that was not significant. This means that it is unlikely that year-by-year increases in baseline ozone have offset significantly the decreases due to UK and European precursor emission controls. This is because baseline ozone levels make a small contribution to ozone levels during the summertime when regional-scale photochemical ozone production and destruction are at their most efficient.

There has been a strong influence from non-linearity between NO_x and VOC. This is apparent because NO_x and VOC emissions have declined by about 40-60% yet peak ozone levels have declined by only 28%. Peak ozone levels fail to reach the 50 ppb level, a level recommended by the World Health Organization (WHO) as an air quality guideline, showing that the level of ambition agreed by the policy-makers has not been adequate and this has had a major impact on the observed downwards trend.

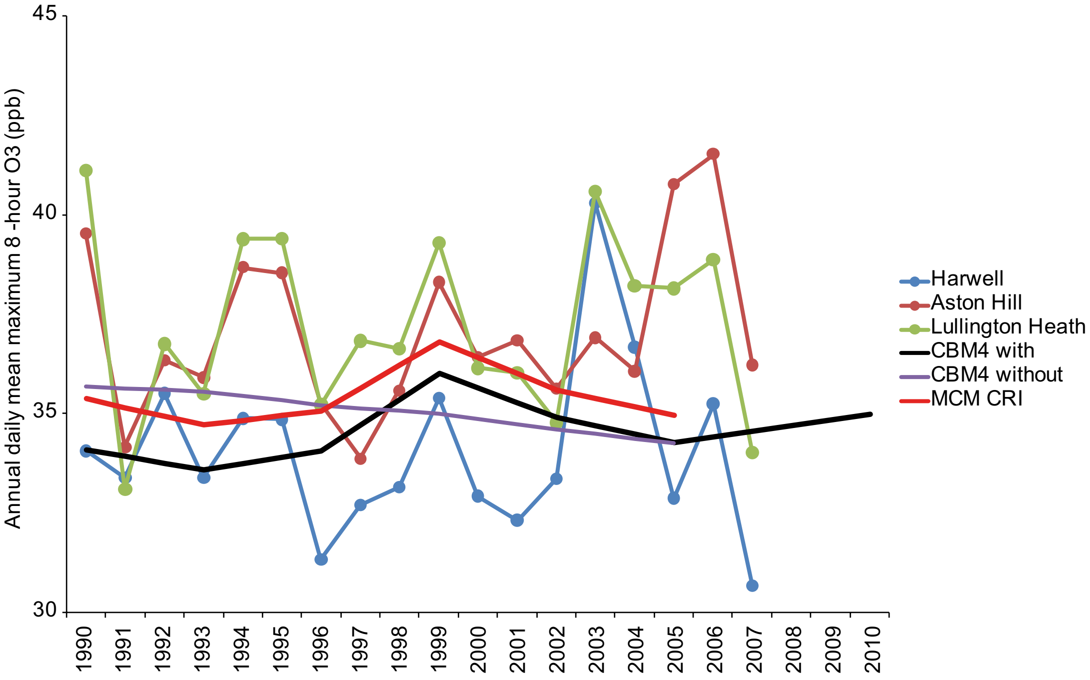


Figure 4.13: Observed (AURN) and modelled (PTM) trends in the annual mean of the daily ozone maximum concentrations from 1990-2010 for locations in the Midlands and south-east England showing the influence of year-by-year variations in intercontinental transport ('With' means with varying intercontinental transport and 'without' means with constant intercontinental transport).

Figure 4.13 illustrates the UK PTM results for the annual mean of the mid-afternoon maximum ozone concentrations using the MCM CRIv2.0 and CBM4 mechanisms. There appears to be no significant difference in the model trends resulting from the choice of chemical mechanism. Year-by-year variability ('with' in Figure 4.13) in intercontinental transport has completely masked the slight downwards trend ('without' in Figure 4.13) due to the reduction in precursor emissions from 1990 to 2005. This latter trend is only slight because of the limited ambition level of the UK and European NO_x and VOC emission reductions agreed.

The balance between the contributions to the observed trends from:

- NO_x and VOC precursor emission reductions
- intercontinental trans-Atlantic ozone transport
- non-linearities in ozone formation
- the ambition level achieved in international policy negotiations,

based on the UK PTM modelling results, appears to be significantly different for the episodic peak and annual mean ozone metrics. All four influences appear to be important to one or other of the ozone metrics.

4.4 Uncertainty

The models described in this chapter and employed in the RoTAP assessment cover a wide range of complexity from the simple statistical Lagrangian trajectory models, such as FRAME and HARM, to the highly sophisticated Eulerian grid-based three-dimensional models, such as CMAQ and EMEP4UK. Models are always incomplete and contain a large number of uncertainties. Uncertainties are introduced into models through the simplifications made in building them, involving the processes of generalisation, distortion, deletion and neglect. Increasing the complexity of models by adding new features and capabilities may be one important way of reducing uncertainties. However, this process of increasing complexity is not without its problems. More complex process descriptions, parameterisations and, indeed, models themselves, may contain more parameters than can be estimated or calibrated with the available observations. Scientific advances will never make it possible to build perfect acid deposition or ground level ozone models. Models will remain simplified and approximate descriptions of the real world and will remain inherently uncertain (National Academy of Sciences, 2007; Oreskes *et al.*, 1994).

Here, attention is given to uncertainties in acid deposition modelling and the reader is referred elsewhere to uncertainties in ground level ozone modelling (AQEG, 2009). The acid deposition models described in this chapter, in common with all environmental models, contain a large number of uncertainties, which for the purposes of discussion may be divided into the following categories:

- simplifications in the model itself arising from theoretical aspects that are not fully understood or from the model parameterisations;
- boundary, initial conditions and other model input data;
- empirical aspects that are difficult or impossible to measure;
- temporal and spatial averaging within the modelling system; and
- limitations of evaluation data and equifinality.

The first area of model uncertainty concerns the theoretical aspects of acid deposition modelling that are not fully understood or processes that are simplified in model parameterisations. This simplifications include: the bi-directional exchange of ammonia, understanding wet deposition and the representation of rainfall events, seeder-feeder effects, orographic and dynamic effects, and chemical interactions, particularly thermodynamic equilibria and the deviations from them in cloud and aerosol chemistry. The lack of theoretical understanding and some of the simplification precludes a definitive choice between the different model approaches, for example Eulerian grid versus Lagrangian trajectory approaches. It also precludes definitive choices between the available parameterisations for meteorological processes, such as rainfall, wet scavenging and cloud-water chemistry, that are adopted in the driving meteorological models used to generate input data for acid deposition models. A review of the uncertainty in specific physical, meteorological and chemical parameters used in simple atmospheric transport models has been undertaken by Abbott *et al.* (2003).

The second area of model uncertainty arises because of the large amount of input data that is used to drive acid deposition models. This includes the boundary and initial conditions for both meteorological models and acid deposition models (if both are utilised). Both the data themselves which may come from observations or other larger area model outputs, and the implementation of them within the acid deposition model have a degree of uncertainty associated with them. Further uncertainty may arise because the process parameterisations used to generate them are themselves approximations of real world behaviour. Wet scavenging coefficients are a good example of this. Rarely are large amounts of highly spatially resolved data available for this purpose and resort is often made to constant drizzle, washout ratios and other approximations. Reliance is often made on global model meteorological and concentration fields without adequate comparison and evaluation.

The third area of model uncertainty concerns those empirical aspects of acid deposition that are difficult or impossible to observe and then to represent in models. Many of the empirical uncertainties involve the measurement of atmospheric concentrations of species such as ammonia, nitric acid, SO_2 and particulate matter (PM) components with adequate spatial and temporal resolution. There are difficulties in specifying cloud-water chemistry and the control that these processes exert on rainfall composition and hence acid deposition. This is a particularly pressing issue for the United Kingdom because of the importance of orographic and seed-feeder effects on acid deposition in upland areas.

The fourth area of model uncertainty arises from spatial and temporal averaging, a feature of all models to a greater or lesser extent. The greater the temporal averaging in a model, the less able it is to take account of aspects of the system that vary with time, because the processes and parameters that drive them are implicitly assumed to be constant over the averaging time considered, when in reality they may be highly variable or sporadic. Scavenging by precipitation is a classic example of a sporadic process. Such processes are not handled well in long-term statistical models. Man-made emissions are most accurately quantified as annual and national totals. These then have to be broken down to an hourly basis and gridded at a spatial scale of 1 km x 1 km across the country. In the real world, the emissions from an individual 1 km x 1 km grid square are highly variable and unpredictable and this inherent variability may introduce significant uncertainty into acid deposition models.

The final area of model uncertainty concerns the limitations of the model evaluation or calibration procedures. Acid deposition models are inherently uncertain representations of real world behaviour and their performance can be evaluated by comparison against observations. In this way, it is straightforward to define an observed deposition field, a model deposition field and a difference field that represents the spatial pattern of the point-by-point discrepancies between the two. This difference field represents the influence of a number of factors including the uncertainties in the model and its input data, together with the local, site-dependent factors that may have influenced the observations. Model parameterisations and input data may be 'tuned' to improve the model field and hence reduce the discrepancies. Indeed, the idea of searching for a single optimal representation of reality is strong in acid deposition and ground level ozone modelling. It is rarely considered that such a description may not be possible or uniquely identifiable. This idea has been called equifinality (Beven and Freer, 2001).

Page *et al.* (2008) recognised the uncertain nature of model deposition fields and used a Generalised Likelihood Uncertainty Estimation (GLUE) framework to choose acceptable sets of model input parameters that minimise the difference field using the HARM model and go on to adopt a probabilistic treatment of critical loads exceedance deposition estimates. This is further discussed in Chapter 5.

4.5 Evaluation of future model requirements

The further development and application of complex Eulerian models to support policy on cost-effective strategies to abate emissions of pollutants is recommended. In recent years models have become powerful tools in the evaluation of a wide range of environmental issues including sulphur and nitrogen deposition, surface ozone, particulate matter and heavy metal deposition. A particular strength of models is their ability to relate pollutant emissions to deposition and concentration and to generate high resolution maps of pollutant concentration and deposition. Models need to demonstrate their accuracy by a robust comparison with measurements.

4.5.1 Future requirements for modelling nitrogen and sulphur deposition

- The application of complex Eulerian models to calculate nitrogen and sulphur deposition in the UK should be supported. The performance of the models should be assessed by comparison with measurements from the national monitoring networks. These should include wet deposition and aerosol concentrations (sulphate, nitrate and ammonium) as well as gas concentrations (SO_2, NO_x, HNO_3 and NH_3). Meteorological models should demonstrate that they can adequately model precipitation, particularly in upland regions. Complex models should be compared with the results from simple models and mapping techniques.
- Complex models should be applied to estimate both future and historical deposition of sulphur and nitrogen, as well as the attribution of deposition to different emissions sources (including national, European and shipping emissions).
- Emissions of SO_2 and NO_x from international shipping make a major contribution to sulphur and nitrogen deposition in the UK. However,

considerable uncertainty surrounds the magnitude of their emissions, spatial location and rate of change. Accurate high resolution maps of emissions from international shipping in the coastal waters of the UK will be employed to support further modelling studies.

- As emissions of SO_2 and NO_x have decreased significantly, the relative importance of ammonia as an air pollutant has increased. High resolution national-scale modelling is necessary in order to capture the local-scale variability of dry deposition of reduced nitrogen.
- Simple models will continue to be useful, in particular concerning source–receptor calculations and uncertainty studies (which require large numbers of model simulations) and for high resolution national-scale modelling studies.

4.5.2 Future requirements for ozone modelling

Ozone models in use in the policy arena should reflect the current state of the art, assess the uncertainties inherent and be able to encompass changes both within the modelling art itself and the expected drivers for future policy.

- There is a requirement to model ozone on an Eulerian basis using chemical schemes tested for ozone, such as the MCM or CBM-IV, that allow robust coupling between the speciation in the emission inventories and the chemical scheme.
- Future ozone concentrations will be influenced by changes on the global and hemispheric scales and policy control measures will increasingly need to be agreed and implemented internationally. The development of modelling tools and systems that are capable of covering spatial scales from urban to global and of addressing air quality and climate change in an integrated manner is recommended.
- As VOC emissions from man-made sources fall, those from natural sources will become more significant. There is therefore a general requirement for improved representation of biogenic species in ozone policy models in order to be prepared for likely warmer summer periods in the future and to be able to better assess any biogenic/anthropogenic coupling.
- There is a need for reassessment of the biogenic emission inventories themselves for the UK.
- It is recognised that spatial and temporal disaggregation of emission estimates is still demanding.
- Model intercomparisons remain a good way to test models and place them in the international domain, coupled to the ongoing necessity for the evaluation of model performance for ozone and its precursors.
- Multi-species models should be explored to give future flexibility to assess multi-pollutant effects.
- Research is needed on biomass burning and its influence on background ozone levels

More details of these recommendations are available in a report to Defra which evaluated and compiled information on the tools for modelling ozone formation and assessed the impacts on human health and ecosystems (Monks *et al.*, 2007).

Chapter 5 Effects on Soils, Freshwaters and Vegetation

Summary

Soils

- Five major soil monitoring programmes show increases in soil pH, primarily in response to the decline in sulphur (S) deposition. A range of factors are identified as affecting the rate of change of soil acidity including soil type, historical S deposition, inherent soil pH, rate of soil carbon (C) accumulation, and past and continuing lime additions. Some studies indicate that recovery may be slower than expected in organic soils as a result of buffering by organic acids.
- There have been reductions in the area of Broad Habitats with critical loads for soil acidity exceeded from 71% of ecosystem area using 1996-98 acid deposition data, to 54% using deposition data for 2006-08; this is predicted to decrease to 40% in 2020. Risks to ecosystems from acidification therefore continue to decline but persist in some areas.
- Topsoil nitrogen (N) concentration has decreased in many habitats despite continued N deposition. A concomitant increase in carbon:nitrogen (C:N) ratios implies that either N loss has increased or that the N signal has been diluted by increased C fixation by plants. There are indications that N deposition has affected soil microbial activity, thus increasing N availability to plants.
- Atmospheric N deposition influences greenhouse gas emissions and C storage in soil and thus climate change. Three large-scale soil monitoring programmes have studied changes in topsoil C concentrations. Two suggested no change whilst one reported major loss. An analysis of possible drivers of spatial patterns for one dataset suggested that reduced S deposition and warmer temperatures could explain some of the temporal and spatial patterns observed. Past changes in land use and management were identified as likely drivers for another dataset.
- The interaction of climate change with air pollution impacts are wide-ranging. One analysis of climate change effects on the area of conifer forests currently receiving deposition of N and acidity in excess of their critical load indicates only a 1-1.5% change in areas at risk of damage. The effect of climate change on biotic stresses such as pest and pathogen attack will be more important for tree growth than change in soil nutritional status. Similar conclusions are drawn from the results of a long-term climate change experiment in heathland.
- The changes observed in soil due to air pollution are coupled with those observed in air, water and vegetation, and together affect a wide range of ecosystem services. These include both positive and negative effects on regulating and supporting services, such as climate regulation, nutrient cycling, regulation of water flow and quality, and support of biodiversity, and on provisioning services such as food and fibre supply.

Freshwaters

- Over the past two decades concentrations of sulphate from non-marine sources (xSO_4^{2-}) in UK acid-sensitive surface waters have declined in line with reductions in xSO_4^{2-} deposition in most regions, although concentrations in the most acidified regions remain several times higher than those in the lowest deposition region in north-west Scotland.
- Nitrate (NO_3^-) concentrations show little evidence of decline and at 2 out of 22 UK Acid Waters Monitoring Network (AWMN) sites concentrations have increased over the last 20 years. Interannual variability is linked to variability in climate. Stable isotope analysis shows that most nitrogen deposition is microbially processed prior to NO_3^- being leached, indicating that, regardless of the oxidised or reduced form, N deposition contributes to freshwater acidity.
- Acid neutralising capacity (ANC) in acidifed waters has increased in proportion to reductions in non-marine SO_4^{2-}. There has been a substantial reduction in the geographical extent and level of exceedance of a biologically-defined critical limit for ANC according to the First-order Acidity Balance model (FAB), although this predicts that the critical load of approximately 27% of the 1752 sites used for mapping purposes will still be exceeded in 2020.
- Increased ANC reflects reductions in hydrogen ions (H^+) (i.e. increased pH) and inorganic aluminium (Al_i) concentrations. Sharp falls in Al_i have occurred in the most heavily acidified streams, particularly with respect to episodic maxima associated with hydrological extremes and sea-salt events. However, Al_i remains substantially above reference levels in the more acidic waters in several regions, and may still represent a barrier to biological recovery here.
- With the removal of much Al_i in more acidified waters, pH is increasing more rapidly than previously in response to continued ANC increases. These sites can be considered to be at a particularly critical stage in their chemical and biological recovery.
- Dissolved organic carbon (DOC) concentrations have increased widely in the UK in an apparent response by soil organic matter to deposition-driven declines in soil acidity, and/or ionic strength, and have partially offset increases in pH predicted by process-based models.
- Surface waters draining managed conifer forests tend to be more acidic than moorland equivalents and recovery to date is more frequently dominated by reductions in Al_i concentration than by pH increases in comparison to neighbouring moorland systems. However, chemical responses are strongly dependent on the stage in the forestry management cycle.
- Evidence of biological recovery in response to improving water chemistry is widespread but communities still differ substantially from those at non-acidified control sites. Biological recovery is expected to lag behind chemical recovery for various physical and biological reasons.
- Comparisons between diatoms in lake sediments and those in sediment traps provide robust indications of the current state of ecological recovery relative to the pre-industrial state. These suggest that in some cases aquatic ecosystems may be developing along new trajectories, possibly due to effects of other drivers such as changing climate or N deposition.

Vegetation

- Critical loads for effects of nitrogen (N) deposition on major sensitive habitats are exceeded for 58% of their area in the UK, and this is expected to decrease to 48% by 2020.
- There is strong evidence that N deposition has significantly reduced the number of plant species per unit area (species richness) in a range of habitats of high conservation value over large areas of the UK.
- The observed loss of plant species richness is primarily due to a decline in frequency of species adapted to low nutrient habitats. In cases where overall species richness has not changed, species characteristic of low nutrient habitats have been replaced by species adapted to higher nutrient availability, with undesirable implications for habitat conservation. There is no evidence of further declines in species richness over the last 20 years in areas of high N deposition, where much of the decline may have preceded the 1980s. However, there is evidence that current N deposition in many parts of the UK is associated with further declines in the frequency of sensitive plant species.
- Taken together, the data from field surveys and experimental studies provide a strong body of coherent evidence that exceedance of critical loads of nitrogen deposition is associated with adverse effects on terrestrial biodiversity at a UK scale.
- There is evidence that the effects of dry-deposited gaseous ammonia are greater than those of the equivalent wet deposition of nitrogen. The critical level of ammonia for lower plants is exceeded over 69% of the UK, and that for higher plants is exceeded over 19% of the UK, and hence ammonia sources should be a priority focus for emission control.
- The changes in ozone exposure that have occurred over the last 20 years in the UK are not captured by the AOT40 index, which represents accumulated exposure over a threshold of 40 ppb. The geographical distribution of recorded field effects of ozone is more consistent with exceedance of critical levels based upon flux into the leaf than critical levels based on AOT40. The AOT40 index is flawed for risk assessment of ozone in the UK, and should be replaced by methods based on modelled ozone flux (POD_Y) into the leaf.
- New POD_Y-based critical levels for indicators of food security, forest carbon storage, fodder quality and vitality of ecosystems of conservation importance have been proposed for use within the Convention on Long-range Transboundary Air Pollution (CLRTAP), but have not been formally adopted.
- Application of POD_Y models that have previously been adopted by CLRTAP for one typical year (2000) suggests that the risk of ozone damage in the UK is higher than estimated using AOT40.
- POD_Y-based critical levels for effects on two major tree species – birch and beech – are exceeded throughout the UK.
- POD_Y-based models estimate that ozone reduced UK wheat production in 2000 by about 1.2 million tonnes, representing a loss of production of 7%. The equivalent figure for potato was 2% of production. Loss of wheat yield varied from 0-15% across the country.
- Production loss estimates based on experimental data do not take account of farm-level factors. Analysis of wheat yield data from cultivar trials in the UK over 15 years has detected a significant effect of ozone, although the size

of the effect was about 50% of that estimated using experimentally-derived relationships with AOT40.

- New experimental data clearly demonstrate that northern hemisphere background concentrations of ozone in the UK have increased to a level where they exceed thresholds for adverse ecological effects on sensitive species from a range of conservationally important plant communities in the UK.
- Although critical loads and levels for effects of N deposition and ozone are widely exceeded in the UK, their combined effects have not been quantified. Important potential effects include those on forest growth and carbon sequestration, which N deposition alone may increase but ozone alone may decrease, and on grassland species diversity, for which both N deposition and ozone in isolation have similar effects on major functional groups.
- N deposition reduces the conservation value of sensitive priority habitats, and is a significant barrier to the UK achieving its targets within the Habitats Directive and Biodiversity Action Plans. Ozone may have similar effects, but there is a much smaller body of supporting evidence.

5.1 Introduction

A wide range of air pollution impacts on ecosystems have been reported (Bobbink *et al.*, 2010). Evidence of specific change for UK ecosystems was reviewed in detail in the NEGTAP report (2001). Here we review new evidence for change in particular ecosystem components, namely the state and function of soils, vegetation and waters, which can be attributed to air pollution. The evidence ranges widely from long-term monitoring programmes to spatial surveys and field and laboratory experiments. These are placed into context through modelling and mapping, with uncertainties specifically addressed and interactive effects of climate change discussed. Sections on the main risk assessment tool, critical loads, which has been the focus of much of the research over the last 20 years, provide a national picture of the change in risk to these ecosystem components since the NEGTAP review in 2001.

The ‘critical loads and levels’ concept is an effects-based risk assessment tool used in the development of pollutant abatement strategies. Critical levels for vegetation are defined as the “concentration, cumulative exposure or cumulative stomatal flux of atmospheric pollutants above which direct adverse effects on sensitive vegetation may occur according to present knowledge”. Critical levels are exceeded when concentrations (or exposure or flux) are above the set critical level. The general definition of a critical load is “a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified elements of the environment do not occur according to present knowledge”. Critical loads may be derived empirically, where the values are based on observed changes in the structure and function of ecosystems (e.g. empirical critical loads of nutrient nitrogen), or using a model-based approach (e.g. steady-state mass-balance models or dynamic models). The model-based critical loads are calculated so that a specified ‘critical limit’ is not violated, for example, to prevent the acid neutralising capacity (ANC) in surface water falling below a specified threshold value, or a concentration of metal in soil increasing above a specified critical limit value. Critical load exceedance is the amount by which pollutant deposition exceeds this critical load. Exceedance of steady-state critical loads represents the potential for harmful effects from pollutant deposition to systems in steady state conditions; thus current exceedance of critical loads does not necessarily equate with current damage. Similarly, achievement of non-exceedance of critical loads does not necessarily mean that affected systems have recovered.

'Dynamic models' are an extension of the critical loads concept, enabling simulations of future trajectories of change in the chemical status of soils or waters under different deposition scenarios, and to estimate the changes required to achieve an acceptable ecosystem status by a given year. The MAGIC model (Cosby *et al.*, 2001; Cosby *et al.*, 1985), one of the most widely used models of soil and water acidification, incorporates an intermediate-complexity representation of the nitrogen cycle. MAGIC is currently used in the UK to model acidity and nitrogen leaching to surface waters. The Very Simple Dynamic (VSD) model (Posch and Reinds, 2009) is similar to MAGIC, but with simpler process representation and lower data requirements. The VSD is designed to run for large numbers of locations via an Access database, which makes it suitable for modelling at a high spatial resolution for terrestrial ecosystems (Chapter 8). VSD$^+$ (Bonten *et al.*, 2009) is an extension of the VSD model with a more sophisticated representation of carbon (C) and nitrogen (N) cycling. The GBMOVE model (Rowe *et al.*, 2009a; Smart *et al.*, 2010) is a static, empirical model which relates soil physical and chemical conditions (which may be generated by MAGIC or VSD), along with information on management and climate, to the probability of occurrence of individual plant species.

The UK critical loads data and outputs from dynamic models (MAGIC, VSD) are submitted to the Coordination Centre for Effects (CCE) for inclusion in European maps and integrated assessment modelling activities under the Convention on Long-range Transboundary Air Pollution (CLRTAP). In the UK, the target of the Thematic Strategy on Air Pollution (CEC, 2005) is no exceedance of critical loads; however, the strategy does not include a timescale to achieve this target.

The critical loads and dynamic models used in the UK are kept under review and updated in accordance with developments in the methods across Europe. For nitrogen, current activities are focusing on:

- A review of the empirical nitrogen critical loads via a CLRTAP workshop (June 2010);
- Deriving critical limits (N concentrations in soil solution) for a wider range of habitats and species for use in steady-state critical load models and the evaluation of scenarios in dynamic models (de Vries et al., 2007; Slootweg et al., 2010)
- The development of integrated dynamic biogeochemical models for calculating critical loads and target loads related to impacts on plant species diversity (e.g. de Vries et al., (2007; 2010); Rowe et al., (2008; 2009a; 2009b); Smart et al., (2010)).

The RoTAP report focuses on the critical loads and dynamic models used to provide a national overview of the areas of habitats at risk from the adverse impacts of acidifying and eutrophying pollutants. The data and maps, derived largely from national-scale input data sets, are appropriate for national-scale assessments but may be less appropriate for site-specific assessments (Hall *et al.*, 2007; Heywood *et al.*, 2007), and do not necessarily include all small areas of sensitive habitats. The freshwater critical loads are largely focused on upland acid-sensitive regions and exclude riparian zones; although these maps are based on data for individual sites they are used to provide a national-scale assessment. At a national scale, simpler models are generally used. These require fewer input parameters than detailed site-specific approaches, involve simplifying assumptions (e.g. soil depth equals depth of rooting zone, percolation is vertical and constant through the soil profile, etc.) and exclude site-specific issues such as topography (e.g. slope) and site-specific management practices. When carrying out assessments of individual sites it is important that site-specific measurement data are used if available to help reduce the uncertainties in the critical loads and exceedances (Heywood *et al.*, 2007; Skeffington *et al.*, 2007). Other aspects of uncertainties are addressed in Section 5.2.4.

In conjunction with the UK conservation agencies and the UK environment agencies a method has been developed to assign 'site relevant critical loads' (SNIFFER, 2007) to the features of designated sites (Special Areas of Conservation (SACs), Special Protection Areas (SPAs), Sites/Areas of Special Scientific Interest (S/ASSIs)). These data are used as a screening tool to identify sites with critical loads exceedance which are therefore potentially at risk from acidification and eutrophication. Results are used to inform the assessment of impacts of 'plans and projects' in relation to the provisions of Article 6.3 of the Habitats Directive and also to inform the UK's air pollution assessment for reporting on 'favourable conservation status'. However, this application of critical loads is not discussed within this report.

5.2 Effects on soils

Soils are an important non-renewable natural resource which contribute to the delivery of essential ecosystem services. These include an important supporting role through nutrient cycling and water regulation for food, fuel and fibre production. Soils also store and filter water, capture and store carbon, and store and emit greenhouse gases affecting delivery of both water and climate regulation. The effects of air pollution on soils can affect soil functioning and thus delivery of some of these ecosystem services. The evidence of change in soil condition and function are reviewed in this section and, together with the evidence from the vegetation and freshwaters sections, the implications for ecosystem services are summarised at the end of the chapter.

The evidence reviewed for soils comes from a series of monitoring programmes and long-term field manipulation experiments. Aspects of soil examined here include changes in soil pH and other measures of soil acidity associated with both sulphur (S) and nitrogen (N) deposition and various components of the N and carbon (C) cycles associated with N deposition. Most data available are for topsoil only. Specific metrics reported include:

- change in soil water sulphate (SO_4^{2-}) concentrations, mostly associated with anthropogenic S deposition and normally the dominant driver of soil and water acidification;
- change in soil pH (the negative logarithm of hydrogen ion (H^+) concentration

with low values associated with acid soils);
- change in the N and C concentrations in the soil and in their relative concentrations (i.e. soil C:N);
- the rate at which the largely unavailable store of soil N is transformed to more available inorganic forms by soil microbes through mineralisation and nitrification processes and various intermediate enzymatic pathways; and
- the rate of N losses as indicated by the change in concentration of N in soil solution and in gaseous fluxes.

Concentrations of metals in soils are reported in Section 6.4.1.

Estimates of change in soil C concentration differ from other metrics in being indirect indicators of air pollution impacts. The changes in soil C concentration result from a change in the balance between carbon inputs to the soil from plants, and carbon losses from the soil due to changes in soil microbial activity or chemical equilibrium. Atmospheric deposition may promote plant growth (e.g. through the fertilising effect of nitrogen deposition) or decrease plant growth (e.g. by the damaging effect of acidic deposition and ozone) (see Section 5.4 for further information). Carbon losses may increase through accelerated decomposition by soil microbes (e.g. if deposition becomes less acidic). We consider the evidence of change as indicated by a change in:

- soil C concentration and density;
- the rate of soil C breakdown as indicated by various intermediate enzymatic pathways; and
- the loss of C and contribution to radiative forcing through change in soil carbon dioxide and methane emissions.

Evidence for changes in dissolved organic carbon (DOC) losses to freshwaters are reviewed in Section 5.3.

A final section provides national statistics and maps illustrating the reduced risk to soils and ecosystems from acidic deposition as a consequence of deposition reduction and thus the effectiveness of emission reduction policies.

5.2.1 Are soils changing? – Evidence from national monitoring programmes

National Soil Inventory

The National Soil Inventory (NSI) provides an unbiased estimate of the distribution of the soils of England and Wales and of the chemistry of the topsoil (0-15 cm) on a 5 km grid (5662 sites) (LandIS, 2010). The first samples were collected between 1978 and 1983. Roughly 40% of the sites were re-sampled at intervals from 12 to 25 years after the original sampling: in 1994/96 for agricultural land and in 2002/03 for non-agricultural land. The same sampling and analytical protocols were used in all the samplings with respect to topsoil pH. Low pH implies high hydrogen ion concentrations, i.e. acidic soils, whilst high pH values are associated with alkaline soils. It should be noted that pH is logarithmic and thus a unit change in pH at the low (acid) end of the pH scale reflects much larger changes in hydrogen concentrations than a unit change at the upper (alkaline) end of the scale. The results show that, in general, topsoil pH increased, i.e. soils became less acid, between the two samplings across both countries under all land uses (Figures 5.1 & 5.2). The magnitude of change was between -0.25 to +1.00 pH units over the 25-year period, a large reduction in topsoil acidity.

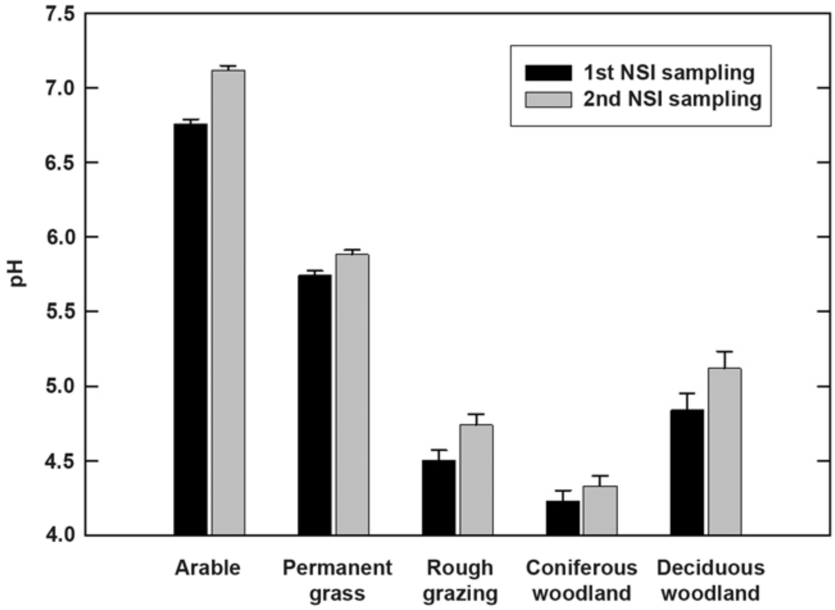


Figure 5.1: Evidence of pH change from the National Soil Inventory of England and Wales (Soil (0-15 cm) pH (in water) by habitat for original (1978-83) and repeat sampling (1994-2003). (LandIS, 2010, Kirk *et al.,* 2010).

In arable land the reduction in topsoil acidity was observed across the pH range, whereas in grassland the main increase was at the acid end of the scale (pH < 5.5) with only a small increase above pH 7. Some part of the change is likely to have been due to changes in land management. This includes better targeting of agricultural lime on acid soils; changes in nitrogen fertiliser use; and deeper ploughing bringing up more calcareous subsoil in soils developed on calcareous underlying minerals. However, statistical analysis of the data has identified decreased acidic deposition as a major driver of change, particularly the approximate 50% decrease in the deposition of acidifying sulphur compounds over the survey period (Kirk *et al.*, 2010).

The statistical analysis assessed the relationship between the rate of change in pH (normalised to an annual basis) and the rate of change in acidic deposition (based on results of the FRAME model for 1970-2005) using a linear regression model, including the effects of topsoil properties (pH, clay content, organic matter content), rainfall and past acid deposition (Figure 5.2). The results for arable land show a significant effect of the change in rate of acidic deposition, though a significant part of the pH increase is not related to the acidic deposition. At sites with a large historical acid deposition, the rate of change for a given change in deposition is greater than at those with lower historical deposition; at sites with higher pH, the rate of change is less than at sites with lower

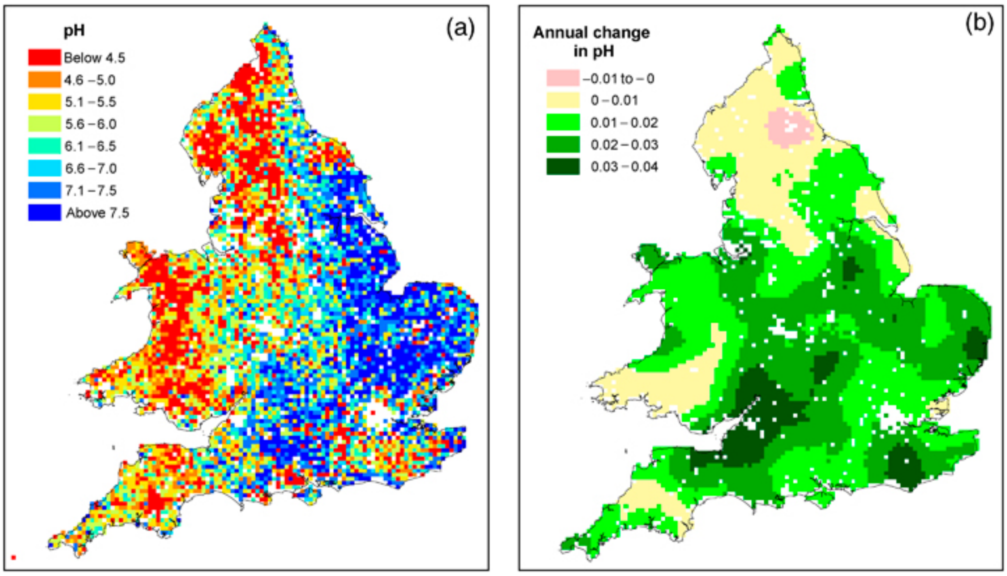


Figure 5.2: Original soil (0-15 cm) pH and annual change for the National Soil Inventory for England and Wales sampled 1978-83 and again in 1994-2003 (Kirk *et al.*, 2010).

pH; at sites with higher rainfall the rate of change is less than at sites with lower rainfall; soil clay content and carbon content do not affect the results. The results for grassland sites are similar, except that the effect of change in acid deposition is only significant in interaction with the historical rate of deposition and the average pH at the site. Effects in other land uses are less clear because of small sample sizes. Whilst coincidental associations cannot be discounted and causal links are difficult to determine absolutely, this study provides strong evidence for recovery of topsoil pH in response to reduced acidic deposition.

Soil (0-15 cm) samples were also analysed for change in organic carbon concentrations. Widespread changes were reported for England and Wales between 1978 and 2003 (Bellamy *et al.*, 2005). Large losses were reported for most land forms over the period although there were gains for soils with low carbon contents. Initially, climate change was thought to be the most likely driver of change because the losses occurred across all types of land use. However, on the basis of expected temperature sensitivity of soil carbon turnover, Smith *et al.* (2007) proposed that only 10-20% of the carbon loss was likely to have been caused by temperature changes. More recently, application of a modelling approach to quantify possible changes in carbon fluxes indicated that climate change effects on temperature and moisture were of sufficient magnitude to explain the observed trends. Past changes in land use and management were more likely explanations for changes in carbon concentrations (Kirk and Bellamy, 2010).

The Countryside Survey

The Countryside Survey is a sample-based study of the UK rural environment. The sample is statistically representative of conditions in the wider countryside, excluding only urban and sea areas. The Countryside Survey provides national and regional estimates of the extent of the different 'Broad Habitats' found in the countryside, plus information on the character and condition of the different vegetation types associated with these Broad and Priority Habitats, including both land and freshwater habitats (Carey *et al.*, 2008). It also provides estimates of the extent and condition of important landscape features such as hedges, walls, ponds and trees, the physical, chemical and biological condition of headwaters, and soil chemistry and biology. Critically these features and characteristics are sampled within the same sample squares at the same time so that relationships between different components of the landscape can be analysed. All reports and summary data can be downloaded from the Countryside Survey website[8]. All methods relating to topsoil measurements can be found in the Countryside Survey Soils Manual (Emmett *et al.*, 2008). Three soil (0-15 cm) samples were collected from each of five random locations (i.e. main plots) within each sample 1 km x 1 km square for a range of chemical, physical and microbial measurements and a single sample (0-8 cm) for soil invertebrate assessment. There were 1197 samples collected from 256 squares in 1978, 1098 samples from the same 256 squares in 1998 and 2614 samples from 591 squares in 2007 for pH and loss-on-ignition testing (a surrogate for measuring soil carbon). Nitrogen analyses were carried out on 1098 samples in 1998 and 1024 samples in 2007. The exact sampling points were relocated to within 2-3 m when squares were revisited. The statistical approach used for analysing the data involved ‘bootstrapping’ which allows for increase in sample number over time.

Mean pH of soil (0-15 cm) across Great Britain increased significantly from 5.39 to 5.67 between 1978 and 1998 with a further increase to 5.87 between 1998 and 2007 (Table 5.1) (Emmett *et al.*, 2010a). At the Broad Habitat scale, fewer statistically significant increases in soil (0-15 cm) pH were observed for the 1998 to 2007 period than for 1978 to 1998. The trend was evident in eight of the ten Broad Habitats for 1978 to 1998 but in only four of the least acidic Broad Habitats (Mixed, broadleaved and yew woodland; Arable; Improved grassland; and Neutral grassland), which are dominated by mineral soils, between 1998 and 2007. The other Broad Habitats, which are more acidic and dominated by organic soils, showed no change between 1998 and 2007, although all habitats, apart from Coniferous woodland, showed a long-term statistically significant increase in pH from 1978 and 2007 as a whole. Patterns were similar when pH data were converted to H^+ concentration. The large annual rate of change in H^+ concentration between 1978-98 for more organic-rich, low pH soils slowed dramatically between 1998-2007, but the smaller initial rate of change in H^+ for high pH, low organic soils was sustained across the 29-year period. Differences in soil acidity trends between soil types/horizons suggest that organic acids may be buffering recovery in the organic soils and/or mineral weathering is contributing to faster recovery in mineral soils/horizons. These trends are consistent with a long-term recovery from acid deposition, although other factors such as liming and fertiliser use on agricultural land are also important in some habitats. N deposition can also acidify in some circumstances depending on the fate and transformations of the deposited nitrogen (see NEGTAP (2001) for a full explanation of this link).

Average soil (0-15 cm) C concentration for all Broad Habitats at the GB scale was 136 g kg^{-1} and 137 g kg^{-1} for 1978 and 2007 respectively, the difference between the two years is not statistically significant (Emmett *et al.*, 2010a). However, this hides a significant 8% increase between 1978 and 1998 and a significant 6% decrease between 1998

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[8] http://www.countrysidesurvey.org.uk

and 2007 (Table 5.1). Many factors can affect soil carbon concentration, including land management, weather variations, climate change and nitrogen deposition. Detailed statistical analysis revealed that change in soil pH is the variable most consistently associated with change in soil carbon concentration (Emmett *et al.*, 2010b) and there is evidence that in turn the change in soil pH is linked to the large-scale decline in sulphur dioxide dry deposition observed in many locations. Some evidence of associations with change in soil carbon concentration were also observed for N deposition (increase in soil C) and some measures of a warmer climate (decrease in soil C) with soil moisture showing the strongest association (increase in soil C) for the 1998-2007 period. No consistent links with above- or below-ground species diversity were observed.

All variables which were significantly associated with topsoil carbon change only explained a component of the variation observed, as there are clearly several drivers acting simultaneously either directly or indirectly on soil carbon concentration. In addition, while the correlations are not proof of causal links, they do follow current scientific understanding (e.g. links between acidity and soil carbon dynamics (Evans *et al.*, 2007; Sanger *et al.*, 1994) and suggest the need to consider the impact of air pollution control policies on soil carbon concentrations.

Table 5.1: Changes in the pH and carbon concentration (g kg^{-1}) of soils (0-15 cm) within Broad Habitats in Great Britain detected by the Countryside Survey between 1978, 1998 and 2007 (Arrows indicate where there is a significant change ($P < 0.05$ level) and direction of change (Emmett *et al.*, 2010a)).

	1978 Mean		1998 Mean		2007 Mean		1978-1998		1998-2007		1978-2007	
Broad Habitat	pH	C	pH	C	pH	C	pH	C	pH	C	pH	C
GB	5.39	135.6	5.67	146.5	5.87	137.0	↑	↑	↑	↓	↑	
Arable	6.59	34.5	6.81	33.5	7.20	30.7	↑		↑	↓	↑	↓
Improved grassland	5.79	56.4	6.06	58.3	6.27	56.9	↑		↑		↑	
Neutral grassland	5.52	67.1	6.00	70.1	6.14	68.0	↑		↑		↑	
Acid grassland	4.43	235.1	4.72	256.7	4.78	228.5	↑			↓	↑	
Mixed, broadleaved and yew woodland	5.08	62.4	5.46	102.2	5.75	88.7	↑	↑	↑		↑	↑
Coniferous woodland	4.33	203.7	4.40	222.0	4.51	197.8				↓		
Bracken	4.16	155.2	4.48	154.7	4.64	195.9				↑	↑	↑
Dwarf shrub heath	4.20	305.3	4.50	298.7	4.55	284.9	↑				↑	
Bog	4.29	411.8	4.49	449.9	4.51	432.9	↑	↑			↑	
Fen, marsh and swamp	4.65	231.7	5.35	252.8	5.46	228.6	↑				↑	

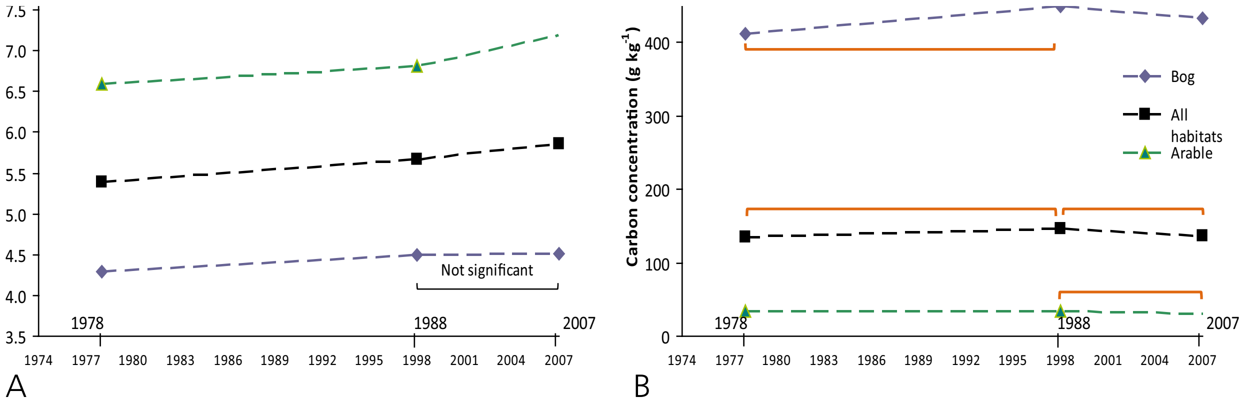

Figure 5.3: Change in soil (0-15 cm) (a) pH and (b) carbon concentration for two contrasting habitat types, Arable and Bog from the Countryside Survey sampled in 1978, 1998 and 2007 (All changes are significant for soil pH except for Bog between 1998 and 2007. Significant changes for soil carbon concentration are shown by brackets, with a small significant increase between 1978 and 1998 and decrease between 1998 and 2007. (Emmett *et al.*, 2010a).

Soil carbon to nitrogen ratio (C:N) is used to indicate N enrichment of soils in semi-natural systems, and, in combination with N deposition rates, to predict nitrogen leaching losses (Dise and Wright, 1995; Gundersen *et al.*, 1998). Results from the Countryside Survey indicate a significant increase in topsoil C:N between 1998 and 2007 with the exception of one Broad Habitat, Arable and horticulture (Emmett *et al.*, 2010a). This suggests that either net primary productivity has increased between the two periods, possibly driven by the trend for increased annual rainfall, resulting in increased quantities of fresh plant material with a high C:N entering the soil, or that an increased proportion of N is being exported in gaseous or dissolved forms possibly driven by the increase in soil pH.

Maps of an index which is more directly relevant to underlying processes of N cycling in soils and N availability to plants (i.e. mineralisable-N) have been reported at a national scale for the first time (Emmett *et al.*, 2010a). Clear geographical patterns were observed which can be used in combination with atmospheric deposition, climate and soil parameters maps in future surveys to determine the consequences of future changes in N deposition on N availability to plants.

Impacts of atmospheric deposition (acidity, N, metals) on biodiversity below ground have not been reported previously at a national scale due to a lack of data. Below-ground diversity comprises a multitude of soil organisms including invertebrates, such as insects, mites, springtails and oligochaete worms, and microbes including bacteria, fungi and archaea. It is of increasing interest partly since it has become clear that species richness below ground far exceeds that in the plant community and because there are new technologies which allow quantification of the microbial element. However, there is limited understanding of the functional importance of below-ground diversity, the link to above-ground diversity, and the impact of major environmental drivers such as atmospheric deposition on the structure and activity of this diverse below-ground community. Significant change in the total catch of soil invertebrates and the number of main taxa was reported for the period 1998-2007 in the Countryside Survey (Emmett *et al.*, 2010a). No link to change in soil C or N was detected at a national scale (Smart, 2010).

Integrated analysis of the full range of variables reported in the Countryside Survey to identify the interdependencies between responses in soil, vegetation and water in response to air pollution, climate and land management is ongoing with an initial report now available (Smart *et al.*, 2010).

Environmental Change Network

The two large spatial soil surveys described above are carried out at approximately 10 to 20 year intervals and therefore do not quantify interannual variability in soil parameters. The Environmental Change Network (ECN) is a network of sites across the UK which provides more detailed information on the temporal dynamics of change in a range of ecosystem properties at some representative sites (Morecroft *et al.*, 2009). Soil solution chemistry may provide a more responsive measure of changes in soil than those available from the two large national programmes which rely on more conventional measurements of soil chemistry; note that surface water trends are reported in Section 5.3. Three non-agricultural ECN sites now have continuous soil solution records for 10 years or more. The three sites are the Moor House blanket peat site in Northern England, and two moorland sites with peaty podzols, Glensaugh and Sourhope, in east-central and south-east Scotland respectively (Sykes and Lane, 1996). The two Scottish moorland sites show similar trends (Figure 5.4). Since sampling began in 1993, sulphate (SO_4^{2-}) concentrations have decreased in both shallow (organic) and deep (mineral) soil horizons, in common with the reductions in SO_4^{2-} in bulk deposition at these sites. Proportionally greater SO_4^{2-} decreases in organic horizons suggest that desorption of sulphur from mineral soils could be slowing recovery, and this is possibly exacerbated by increased fluxes from upper organic horizons due to increased pH. Sourhope has moderate inorganic N leaching (O horizon mean 10 $\mu eq\ l^{-1}$), with a peak in the late 1990s. Glensaugh has lower concentrations (O horizon mean 5 $\mu eq\ l^{-1}$) but these appear to have increased since 2003. Both sites show clear evidence of reduced acidity and therefore recovery in mineral horizons, but no overall change in the (more acid) organic horizons. This pattern corresponds closely to the patterns observed in the Countryside Survey and those of the ICP Level II sites reported below, suggesting common behaviour across a range of mineral and organo-mineral soils. Although a number of explanations are possible, one contributing factor appears to be that rising DOC, and hence organic acid, concentrations have offset the decline in SO_4^{2-}, buffering pH change. Buffering is likely to be greater in high-DOC organic horizons than in mineral horizons (and subsequently in drainage waters) due to mineral soil DOC retention and/or mineral weathering aiding recovery in mineral horizons. Data from control plots at the Centre for Ecology and Hydrology (CEH) Clocaenog experiment, a heathland podzol site, also show greater pH recovery in the mineral horizon over a 10-year period (Sowerby *et al.*, 2010).

Unlike the podzol sites, Moor House data show near-linear pH increases at both depths in the blanket peat since 1992. Remarkably, this has occurred without any change in soil solution SO_4^{2-} and nitrate (NO_3^-), which are mostly below detection limits. Instead, the principal driver of pH recovery at Moor House appears to be a major decrease in chloride

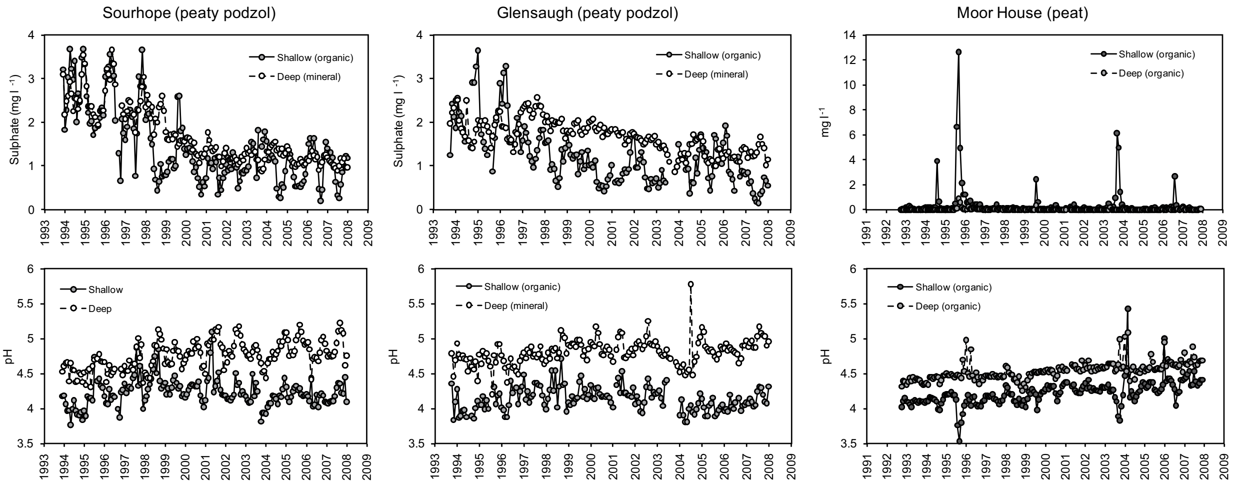

Figure 5.4: Time series of sulphate and pH in soil solution samplers at three moorland ECN sites (Data represent monthly mean concentrations for six samplers.). Source ECN (http://www.ecn.ac.uk/).

(Cl$^-$) concentrations (Figure 5.5). Although this could be attributable to reduced sea-salt deposition since the early 1990s, the sustained nature of the decline, and the clear increase in the sodium:chloride ratio makes such a climatic driver unlikely. Furthermore, between 1990 and 2006, UK hydrogen chloride (HCl) emissions declined by 94% (Dore *et al.*, 2008); a substantial fraction of HCl is deposited close to emission sources (primarily coal burning), but may be transported to more remote locations if captured in cloud droplets or aerosol. The Moor House data suggest that HCl deposition could be an important factor here, and potentially at other remote locations. Many other ECN and UK Acid Waters Monitoring Network (AWMN) sites exhibit declining Cl$^-$ concentrations; the relative importance of climatic (sea-salt deposition) and anthropogenic (HCl deposition) drivers of these decreases is uncertain. HCl is a particularly potent acidifier in peats because, unlike SO$_4^{2-}$ or NO$_3^-$, Cl$^-$ is not subject to reducing processes, and is therefore highly mobile. Perhaps surprisingly, given the scale of emissions reductions, HCl deposition has received little previous attention in assessments of recovery from acidification, and is omitted from current critical load exceedance calculations and dynamic models.

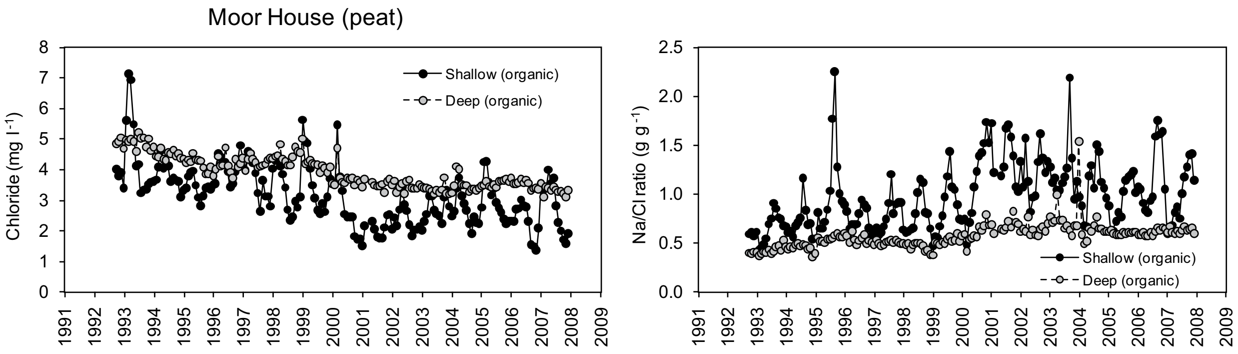

Figure 5.5: Time series of chloride, and the ratio of sodium to chloride, at Moor House ECN site (Data represent monthly mean concentrations for 6 samplers. Source ECN (http://www.ecn.ac.uk/).

International Co-operative Programme (ICP) – Level II Intensive forest monitoring

Temporal trends in soil solution

Long term trend analysis of the rainfall, throughfall and soil solution elemental fluxes from 12 years of monitoring at ten ICP Level II intensive forest monitoring sites in the UK reveal coherent national chemical trends indicative of recovery from S deposition and acidification. The recovery is confirmed by pH increases and SO_4^{2-}, aluminium and manganese decreases in the soil solution at most of the sites. Soil pH only increased at sites which had been polluted historically such as Sherwood in the south Pennines and Llyn Brianne in Wales, again the magnitude of increase is higher in the mineral soil than the organic soil (Figure 5.6). Trends in soil solution N concentrations were variable and dependent on the form of N. Nitrate in soil solution declined significantly at two sites only, Thetford in East Anglia (receiving high N deposition from local agricultural, mainly livestock, sources) and Sherwood. In contrast, increases in dissolved organic nitrogen (DON) observed in five out of the ten Level II sites seem to be a direct response to increased rainfall and throughfall DON. Significant increases in DOC concentrations were detected in the soils at some sites, which may be a response to declining air pollutant inputs and/or climate changes. Significant declines in soil solution calcium:aluminium (Ca:Al) molar ratios were observed in the majority of sites, reflecting in most cases a Ca decline rather than an Al increase (Vanguelova *et al.*, 2010). Detailed environmental analysis at some monitoring sites suggests the importance of insect infestations in forests on nutrient and carbon cycling (Pitman *et al.*, 2010).

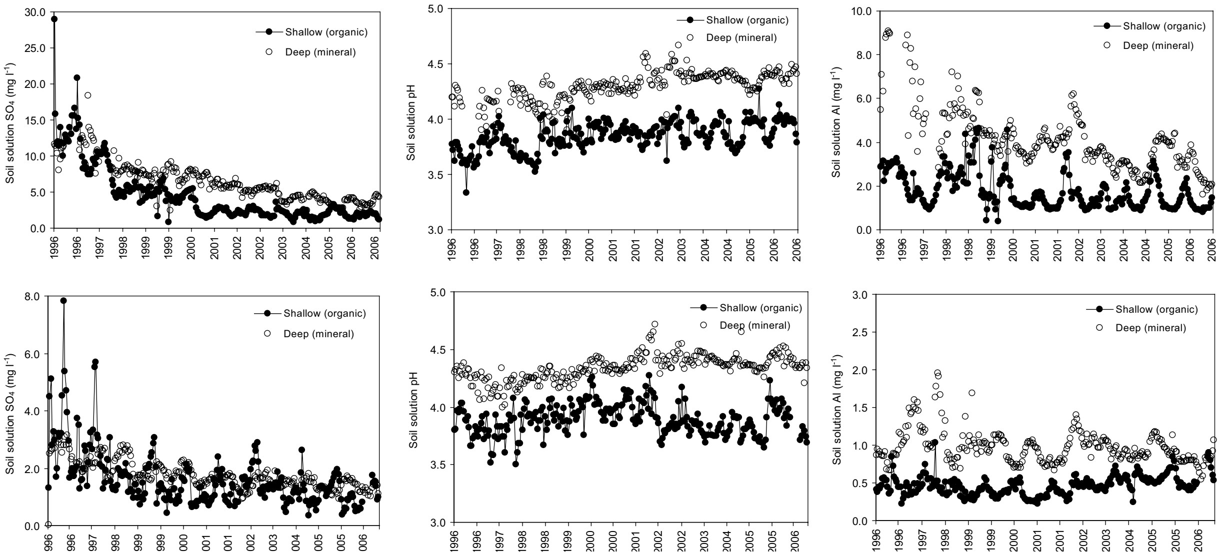

Figure 5.6: Time series of sulphate, pH and aluminium in the soil solution at Sherwood (top three graphs) and Llyn Brianne (bottom three graphs) Level II forest monitoring sites (Vanguelova *et al.*, 2010).

Temporal trends in soil

The soils at four upland Sitka spruce Level II sites sampled in 1995 were resampled in 2008. Two of these sites (Coalburn in northern England and Llyn Brianne in South Wales) are on highly organic peaty gley soils while the other two (Tummel and Loch Awe, both in Scotland) are on sandy podzolic soils. No change in pH in organic soil horizons was detected at any of the sites; there was an increase in soil pH from 4.03 to 4.37 in the upper A mineral soil at Coalburn and from 4.3 to 4.5 in the mineral Bg horizon at Llyn Brianne consistent with the soil solution trends in recovery seen from the ECN and Level II mineral soils. An increase in total N in the soil F layer and a decline in C and N in the peat H layer at both Coalburn and Llyn Brianne were detected at sites where significant increase in soil solution DOC and NO_3^- for the last 6-10 years has also been observed (Vanguelova *et al.*, 2010). Frequent impacts of aphids at these sites were recorded and their impact on canopy defoliation which contributed to the increased water flux and canopy-derived DOC and N (Pitman *et al.*, 2010). These detailed studies have shown the complexity of forest ecosystems and the need to evaluate all biotic and abiotic factors when assessing pollution impact on forest soils.

ICP – Level I and BioSoil soil monitoring (167 forest sites across UK)

Spatial trends

The soil C and N stocks in forest soils were estimated from 167 sites from the BioSoil survey of forest soils which is part of the EU ICP forests. The total averaged C and N content in forest soils, up to 80 cm soil depth, across Great Britain ranged between 132 and 448 t C ha^{-1} and 6 and 19 t N ha^{-1}, respectively. The soil C and N content varied with soil depth, soil type, forest type and stand age. Both C and N soil stocks across the different soil types decreased in the order deep peats > peaty gleys > groundwater gleys = surface water gleys > podzols and ironpans = brown earths > rankers and redinas. Litter and F horizons store on average 9 and 13 t C ha^{-1}, and 0.3 and 0.6 t N ha^{-1} respectively and could add substantially to the overall soil C and N stocks in forest soils (Vanguelova, 2010). The range of forest organic layer C:N is between 16 and 42 under coniferous forests plots and between 15 and 29 under broadleaved forests, with ratios below 25 in 60% of coniferous plots (94 plots in total) and in nearly 90% of the broadleaved plots (73 plots in total) (Vanguelova, 2010).

Woodlands Survey

In 1971, 103 woodlands across Britain were selected as representative of a wider sample of 2453 woodlands (>4 ha) surveyed in the late 1960s. Within each of the 103 woodlands sixteen 200 m^2 plots were located at random and records made of soils, tree and shrub composition, and ground flora with each plot. Between 2000 and 2003 (the '2001' survey) the sites were revisited and the plots re-recorded as close to the same point as possible with the original recording, sampling and analytical methods used throughout. Soil samples were obtained from every accessible plot in every woodland. Samples (of about 1 kg) were taken to a depth of 15 cm with subsequent analyses carried out using standard methodologies (Allen, 1974) and quality control procedures. The results from the 2001 survey were compared with the original data and changes identified at plot and site levels.

Overall there was a significant increase in soil pH, with a mean magnitude of change of +0.33 units over the 30-year period. Soil carbon content (g kg^{-1}) at a GB level however did not change significantly during this period. Table 5.2 summarises soil pH values in both survey periods with mean changes in soil pH at the GB level and for soil pH and soil organic matter classes. The greatest increases in soil pH were manifest in mineral soils, and in particular the most calcareous soils.

Table 5.2: pH values of soils in the Woodland Surveys (Soil pH and organic matter classes were derived from values in both survey years to minimise effects of regression-to-the mean). (Kirby *et al.*, 2005).

	mean soil pH values		mean change in soil pH	sample N
	1971	Resurvey		
GB level	4.98	5.31	0.33	1618
By soil pH class				
4.5≥pH	4.02	4.26	0.24	594
4.5<pH≤6.6	5.16	5.48	0.33	817
6.6<pH≤7.3	6.68	7.17	0.48	100
7.3<pH	7.47	8.17	0.70	107
By soil organic matter class				
mineral	4.95	5.33	0.39	371
organo-mineral	5.09	5.41	0.32	995
organic	4.61	4.90	0.29	248

Statistical analysis, using an analysis-of-variance mixed-modelling approach, was used to review relationships between soil pH changes and changes in a range of pressures and drivers, including atmospheric N and S deposition (based on revised FRAME model data for 1986, 1996 and 2006), climate change and management influences. The best predictors of the observed changes in soil pH were the changes in total S, wet NO_3^- and wet ammonium (NH_4^+) deposition (1986 to 2006) along with changes in basal area of trees and soil organic carbon (1971 to 2000). Increasing soil pH was related to locations where S deposition and wet NH_4^+ deposition had declined the most and also to where S deposition levels were the highest during this period. A positive relationship between change in soil pH and change in wet NO_3^- deposition (i.e. soil pH increased most where deposition has changed least) is more complex to interpret and may be related to the relatively high levels of historical deposition in locations where the greatest declines in wet NO_3^- have been estimated. It would also appear that soil organic carbon and tree growth are influencing soil pH in the opposite direction to the GB-level trend. Although there was a general increase in soil pH across GB, this increase was less distinctive where trees had grown most and, correspondingly, where soil organic carbon content had increased. Vegetation analyses from the same survey indicate an overall trend in eutrophication of ground flora. These results suggest a complex interaction between the direct and indirect impacts of acidification and eutrophication on soils but clear evidence of increases in soil pH since 1971 as for all other broad-scale surveys.

Synthesis of large-scale surveys

These national surveys with repeated samplings provide some consistent messages particularly with regard to the increase in soil and soil water pH and a reduction in soil SO_4^{2-} concentrations, indicating a reduction in the acidity of soils (Table 5.3). Statistical analysis has clearly linked this to the decline in sulphur emissions, demonstrating this is a major benefit of the emission controls which have been in place for the last 30 years. The trends for nitrogen are unexpected and further work is required to interpret results, in particular the links to changes in the C cycle.

With regard to C, the evidence is directly contradictory, with two studies indicating no overall change at a GB level since the 1970s and one reporting a major decline. Analysis is ongoing to attribute trends observed but the reasons for the different trends reported remain unclear (Smart, 2010; Smith *et al.*, 2007).

Table 5.3: A summary of significant temporal trends observed in major large-scale monitoring programmes (Arrows indicate significant change in direction shown; a '–' indicates measured but no significant change).

	NSI	CS	CS2	ECN	ICP Level II	Woodland Survey	Comments
Years	1978/83–1994/2003	1978–1998	1998–2007	1993–2008	1996–2008	1971–2000/03	
Spatial coverage	England and Wales	Great Britain	Great Britain	Great Britain	Great Britain	Great Britain	
Depth of soil or soil water sampled	0-15 cm	0-15 cm	0-15 cm	Soil water in organic and mineral horizons	Soil water in organic and mineral horizons	0-15 cm	
No. of sites	1978/83 = 5662 1994/2003 = 2179	1978 = 1197 1998 = 1098	1998 = 1098 2007 = 2614	3 sites over >10 years	10 sites over 12 years	103	
Soil pH	↑	↑	↑			↑	Increase suggests recovery in response to reduced acidic deposition. Increase generally clearer in mineral soils.
Soil N			↓				Unexpected decrease suggests ongoing N deposition may be diluted with extra C fixation or N exported.
Soil C	↓	↑	↓			–	Increases indicate an increase in plant production usually in litter layer. Range of drivers of spatial and temporal trends identified, including decreased acidity, climate, and land use and management.

	NSI	CS	CS2	ECN	ICP Level II	Woodland Survey	Comments
Years	1978/83–1994/2003	1978–1998	1998–2007	1993–2008	1996–2008	1971–2000/03	
Spatial coverage	England and Wales	Great Britain	Great Britain	Great Britain	Great Britain	Great Britain	
Soil C:N			↑				Increase suggests increased C fixation or increased N loss in excess of N deposited.
Soil water pH				↑	↑		As for soil pH.
Soil water sulphate concentration				↓ mineral = peats	↓		A decrease indicates response to declining sulphur deposition. Signal generally stronger in mineral soils.
Soil water inorganic-N concentration				-	Variable		Increase suggests increase in N lost in drainage water due to N enrichment of soil by N deposition. Fertiliser use generally not relevant for sites studied.
Soil water DON concentration					↑		Increase suggests increase in N lost in drainage water due to N enrichment of soil by N deposition. Fertiliser use generally not relevant for sites studied.
Reference	1	2	2	3	4	5	

References: 1. Kirk et al. (2010); 2. Emmett et al. (2010a); 3. Morecroft et al. (2009); 4. Vanguelova *et al.* (2010); 5. Kirby *et al.* (2005)

5.2.2 Are soils changing? – Evidence from experimental and gradient studies

Data from nine long-term N manipulation experiments and five gradient studies have been collated to test the evidence for changes in ecosystem function. Gradient studies consist of sampling programmes which span deposition gradients at the regional or national scale. Their value lies in their relatively low cost compared to larger surveys which may not be focused on the issue of interest, e.g. N deposition. Statistical analysis is used to identify relationships with a range of environmental gradients including atmospheric deposition (Table 5.4). Causal relationships cannot be inferred from the survey data alone but can be used in combination with experimental studies and national monitoring programmes to support findings of direct links. Many of the gradient studies and most of the experiments are part of the UKREATE consortium[9].

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[9] Further information can be found at http://www.bangor.ceh.ac.uk/terrestrial-umbrella/.

All experimental studies reported here are plot-based experiments within semi-natural habitats of conservation value for which new data has become available since NEGTAP (2001). The value of experiments is that other factors such as climate and land management are kept constant and therefore causal links to changes observed can be made; however, due to the cost of maintenance over a long time period, the number of experiments is limited. All experiments reported here have received chronic N applications (for more than 5 years) in small frequent doses. The form and dose of N applied (reduced/oxidised and wet/dry) differ and there is variability between the sites in terms of response to N additions both within and between habitat types. Many sites indicate an acceleration of the N cycle and increased availability of N within the system as observed in the national monitoring programmes (Section 5.2.1). The response of the vegetation is described in Section 5.4.

Table 5.4: Summary of responses observed in a series of spatial survey and nitrogen deposition gradient studies (Arrows indicate significant change in direction shown; a '–' indicates measured but no significant change).

	Acid grassland survey	Upland heathland survey	Lowland heathland survey	*Racomitrium* heathland survey	Sand dune survey
Soil pH	↓	–	–	–	
Soil N	–	↑	↑	–	–
Soil/litter C				–	–
Soil C:N				↓	↑
Soil water pH	↓				
Soil water sulphate concentration					
Soil water inorganic-N concentration	↑	↑			
Potential net nitrogen mineralisation					↓
Litter depth			↑		
Litter N			↑		
Litter P			↑		
Litter phenol oxidase		↓			
Litter PME			↑ with N_{ox} and N_{red} (not N_{tot})		
Soil PME			↑ with N_{ox} and N_{red} (not N_{tot})		
Soil phenol oxidase			↑ (N_{ox})		
Reference	1	2	2	3	4

References: 1. Stevens *et al*. (2006); 2. UKREATE (2010); 3. Armitage (2010); 4. Jones *et al.* (2004)

When reviewed together, the results from the experimental and gradient studies show increased storage of N in the soil, acceleration of the N cycle (mineralisation and nitrification) releasing inorganic N from the soil store (extractable NH_4^+ and NO_3^-) and

Table 5.5: Summary of responses observed in soils in a series of nitrogen addition experiments (UKREATE, 2010). (Arrows indicate significant change in direction shown; a '–' indicates measured but no significant change).

	Ruabon upland heath	Budworth lowland heath	Thursley lowland heath	Culardoch low alpine heath	Whim bog Wet Dry	Wardlow calcareous grassland	Wardlow acidic grassland	Pwllpeiran acidic grassland	Newborough fixed sand dune
Soil N	↑	↑	↑	↑	↑	-	-	-	-
Soil C:N	↓	↓	↓	↓	- -			-	-
Soil NH_4^+ and NO_3^-	↑	↑	↑	↑	↑ ↑	↑	↑	↑	-
Inorganic N leaching	↑	↑	-	↑	↑ ↑	↑	↑	↑	
DON leaching	-			↑		-	↑	-	
Soil water pH				↓					
Potential net N mineralisation	↑		↑ -	-	- -	↑	↑	-	↑
Potential net nitrification	↑		-	-	↑ ↑	↑	↑	-	
Ammonium and nitrate pool turnover rates (O)	-	↓	-				↓	-	
Gross ammonification and immobilisation	-	-	-				-	-	
Gross nitrification and immobilisation (O)	-	-	-				↓	-	
Soil pH			-	-	↑ (NO_3^-) = (NH_4^+) ↑ (NH_y)	-	-	↑↓ (dependent on N form)	-
Reference	A	B, C	D	E, F, G	D	H, I, J,		K	L

References: A. (Pilkington *et al.*, 2005); B. (Wilson, 2003); C. (Ray, 2007); D. (UKREATE, 2008); E. (Britton and Fisher, 2008); F. (Papanikolaou, 2008); G.(Helliwell *et al.*, 2010); H. (Horswill et al., 2008); I. (Phoenix *et al.*, 2003) J. (Morecroft *et al.*, 1994); K. (Emmett *et al.*, 2004); L. (Plassmann *et al.*, 2009);

increased leaching losses. However, this generalisation is not universal. In carbon-poor, N-limited systems where plant growth is stimulated by the added N, the increase in plant N uptake will cause an increase in production of plant material rich in C which is incorporated into the soil, effectively 'diluting' the N signal and slowing the N cycle. This is seen most clearly in the sand dune gradient study where N stimulated plant production and led to an increase in soil C:N ratio, and a decrease in available N (Jones *et al.*, 2004). It could be argued this increased storage of C is beneficial for climate regulation, an important ecosystem service. The variability in responses, when not related to the form of N, may be related to the different N status of the systems prior to treatments starting. A conceptual model, attempting to integrate the sequence of responses which may be expected as soil N availability increases, is illustrated in Figure 5.7. This model, which is based on evidence from a range of studies, is described in more detail by Emmett (2007), who adapted the sequence proposed by Aber *et al.* (1989).

Using the stages of the conceptual model shown in Figure 5.7, the dune system may be at an earlier stage of N enrichment or saturation, i.e. Stage 0-1 showing no change in soil C:N or N leaching in response to N addition. In contrast, the heathland sites at Ruabon

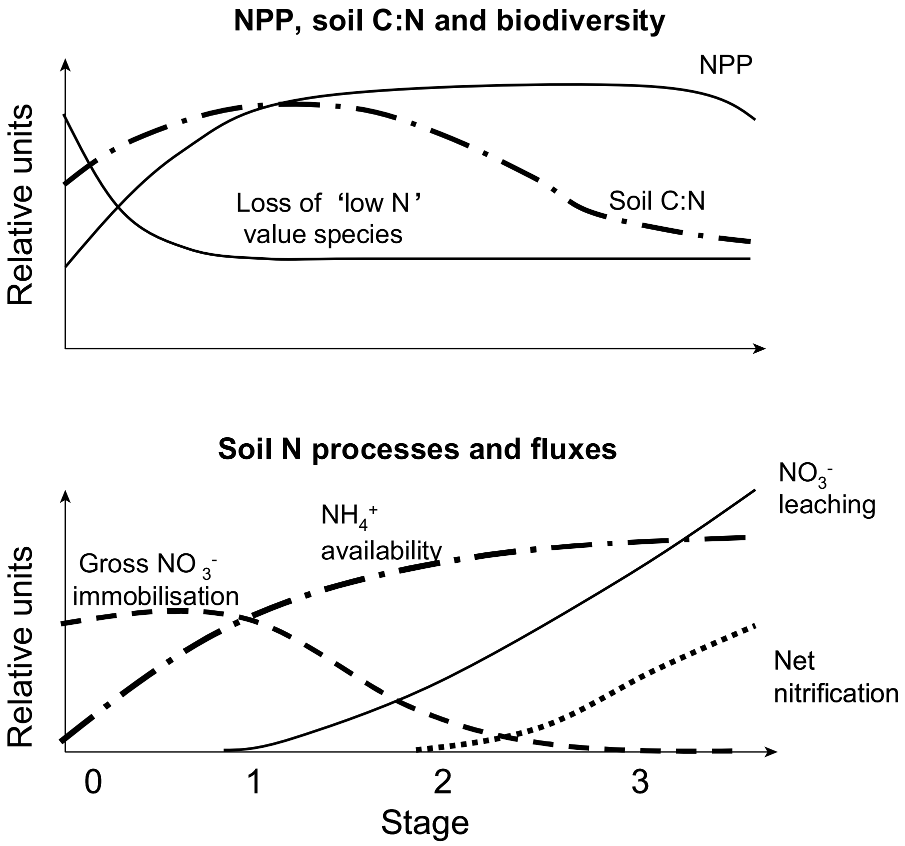

Figure 5.7: Conceptual model illustrating the relative rate of ecosystem processes across a nitrogen availability gradient (Emmett, 2007) (Processes included are: net primary production (NPP), rate of loss of plant species which favour low N availability and different aspects of the N cycle. Experimental sites can be at different stages due to different inherent fertility and/or historical N deposition. Responses to N applications may therefore be variable due to different initial baseline conditions).

and Budworth, the low alpine heath at Culardoch and the heathland at Thursley are at Stage 1-2 with reductions in soil C:N and N leaching in response to N additions. The grassland sites at Wardlow and Pwllpeiran are at Stage 3, resulting in less change in soil C:N, as most of the N is leached and not retained in the soil.

These temporal dynamics underline the complexity of the N cycle and the problems of identifying national-scale trends within large-scale monitoring programmes. While there are some similarities between the national monitoring programmes, gradient studies and experimental studies, the various inconsistencies reflect the influence of different baseline conditions, historical and current form and rate of N deposition, variable climate conditions and land management. The latter two are discussed in more depth below.

Declines in pH can be dependent on the current N status of a site as this determines the rate of certain soil N transformations and uptake patterns which drive the acidification process. One of the most important acidifying processes is the rate of nitrification, i.e. the conversion of ammonium (NH_4^+) in the soil to nitrate (NO_3^-) by soil microbes:

$$NH_4^+ + 2O_2 = NO_3^- + H_2O + 2H^+$$

As can be seen, acidity (H^+ ions) is produced each time NH_4^+ is transformed to NO_3^-. Nitrification generally increases with N enrichment of a site and thus as NH_4^+ supply for the microbes increases. The rate of nitrification is generally higher in high pH soils which buffer the acidity produced but NH_4^+ supply appears to be the dominant factor as there are many studies demonstrating high rates of nitrification in acid soils due to the diverse range of organisms for this process, e.g. Nicol *et al. (2008)*.

At the experimental sites, the effect of N addition on soil pH is dominated primarily by the form of N applied and whether the N is combined with SO_4^{2-} applications. Soil pH always declines if ammonium sulphate has been applied. Ammonium itself contributes to an increase in acidity depending on the fate of the NH_4^+ and the NO_3^- produced (e.g. (Pilkington *et al.*, 2005; van Breemen *et al.,* 1982). If NO_3^- is taken up by plants or microbes and is not increased in soil solution then NH_4^+ itself will not cause a decline in soil pH. This probably explains the lack of soil pH change in the wet-deposited NH_4^+ treatment in the bog experiment at Whim. In the dune study there is again no change in NO_3^- leaching and thus no change in soil pH is observed. As the site is N-limited, N is stored rather than becoming available for the nitrification and leaching processes that contribute to acidification.

How do these results for soil pH relate to those from the national monitoring programmes? Statistical analysis clearly shows that the large decline in sulphur deposition since the 1980s is the major cause of the increase in soil pH (i.e. recovery) reported by the national monitoring programmes. There has not been a consistent countrywide decline in N deposition since deposition monitoring started in 1986 and this therefore cannot have contributed to the recovery of soil pH at the national scale. Indeed, the evidence from the experiments emphasises the potential of chronic nitrogen deposition to slow the rate of recovery in locations where N transformations in the soil and NO_3^- leaching have been stimulated. This risk of soil acidification in response to continuing levels of nitrogen deposition increases with time as the soil becomes further enriched with nitrogen.

5.2.3 Is there a reduction in risk to soils from air pollution due to reduced emissions? – Critical load exceedance and uncertainties for acidity

The critical load approach is a risk assessment effects-based tool which identifies the rate of deposition at which long-term damage to sensitive parts of an ecosystem is likely to occur according to current knowledge. Critical loads provide effective simplification and a predictive tool enabling information to be transferred in a useful format to environmental managers and policy-makers. A working definition provided by Nilsson and Grennfelt (1988) is:

> "A quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge."

It must be emphasised that critical loads do not describe actual changes which have taken place – they are a risk assessment tool without timescale. In some cases damage may already be in progress whilst in areas which have received less pollution to date or which have greater internal buffering, change may not occur for many years.

To date simple steady-state mass-balance models and empirical data have been used to set nutrient N and acidity critical loads for Europe. Combined with spatial datasets these critical loads have been used to identify areas at risk from acidification and atmospheric N deposition. The benefits of this approach compared to emission-based, cost–benefit or transboundary limit approaches is that it is effects-based and geographically explicit, so areas at potential risk from pollutant deposition can be identified and the likely direction and, in some cases, magnitude of changes recognised. The concept is also simple enough to be universally applicable and widely understood by non-specialists whilst the data required are often available at the broad regional scale. For the UK, critical loads are calculated and mapped for terrestrial Biodiversity Action Plan (BAP) Broad Habitats that are sensitive to acidification and eutrophication, and for which sufficient data exist to map their distribution nationally. For surface waters the critical load maps are based on 1752 sites sampled across the UK. Eutrophication critical loads are presented in Section 5.4.5. Acidity critical loads for terrestrial systems are presented here.

Different methods are used to calculate acidity critical loads for different habitats in the UK. An empirical approach, based upon the mineralogy and weathering rate of the dominant soil in each 1 km x 1 km square is applied to non-woodland habitats on mineral or organo-mineral soils (Hornung *et al.*, 1995). For woodland habitats, a simple mass-balance (SMB) model is applied that balances the acidic inputs to and outputs from a system to derive a critical load that ensures a chosen critical chemical limit is not exceeded (Langan *et al.*, 2004; Sverdrup and de Vries, 1994). Where habitats occur on peat soils, the critical load is based on the amount of acid deposition that would prevent the soil solution pH falling below pH 4.4 (Calver, 2003; Calver *et al.*, 2004; Skiba and Cresser, 1989). These methods provide critical loads for systems at long-term steady state. Exceedance of these critical loads therefore demonstrates the *potential* for harmful effects to a system at steady state.

Deposition of both S and N compounds can contribute to exceedance of acidity critical loads. The Critical Load Function (CLF), developed under the CLRTAP (Posch *et al.*, 1995), defines combinations of S and N deposition that will not cause harmful effects. This requires the calculation of three acidity critical load values: the 'maximum critical load of sulphur' (i.e. the critical load in terms of S only (if N deposition was zero), taking into account base cation deposition to the soil system and base cation removal from the system), the 'minimum critical load of nitrogen' (i.e. the sum of the long-term N processes in the soil: removal and uptake by vegetation, N immobilisation and denitrification), the 'maximum critical load of N' (i.e. the critical load if S deposition was zero). These critical load values are calculated for mapped 1 km x 1 km squares of Broad Habitat sensitive to acidification using soil- and habitat-specific parameters. A detailed description of the methods and data currently being used in the UK can be found in Hall *et al.* (2003; 2004a). Calculations of exceedance have shown reductions in the area of Broad Habitats exceeded, from 71% using 1996-98 acid deposition data, to 54% using deposition data for 2006-08; exceedance is predicted to decrease to 40% in 2020. The maps in Figure 5.8 show the results for 1996-98 and 2006-08.

One major source of confusion about interpretation of the critical load maps is how maps can show continuing large areas of acidification risk when a trend of recovery is seen in soil pH in many of the studies reported here. This is because acidification is a dynamic process. Acidic deposition may decrease thus enabling soil pH to increase towards the 'pristine' state but still remain below that required to protect sensitive components of the ecosystem and thus be exceeded with respect to the critical load.

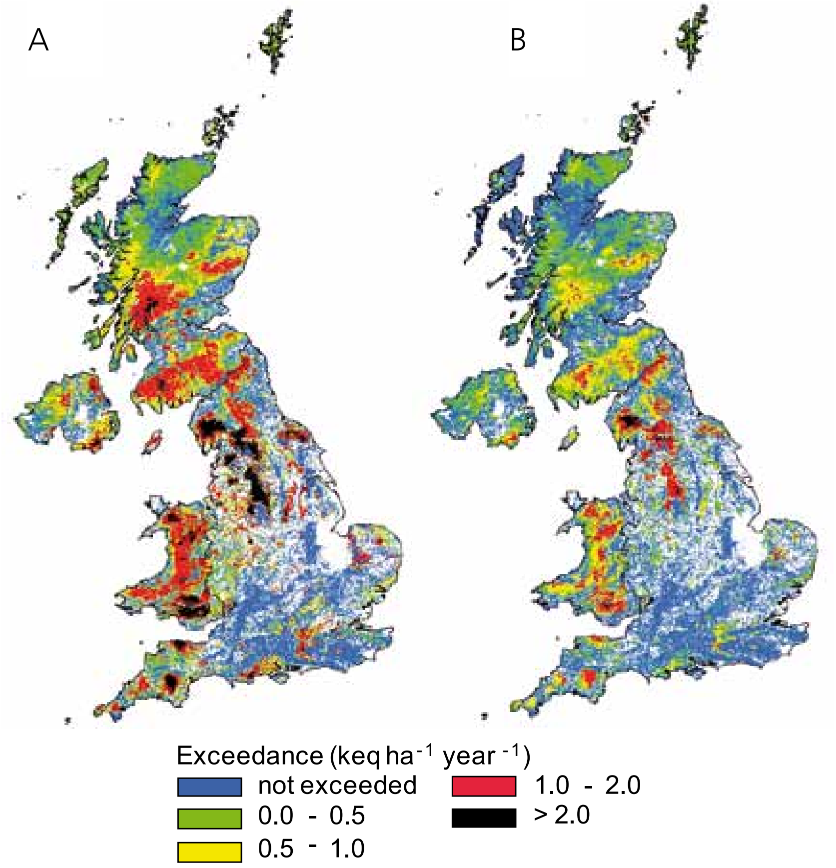

Figure 5.8: Exceedance of 5th-percentile critical loads of acidity by acid deposition for (a) 1996-98 and (b) 2006-08. Source CEH/RoTAP.

5.2.4 Uncertainties in the risk assessment approach used for impacts of air pollution impacts on UK soils

Uncertainties in the critical loads approach have been the subject of extensive research over the last decade (Barkman, 1998; Barkman and Alveteg, 2001; Hall *et al.*, 2001; Hall *et al.*, 2004b; Heywood *et al.*, 2006a; Heywood *et al.*, 2006b; Heywood *et al.*, 2006c; Hodson and Langan, 1999; Langan *et al.*, 2001; Skeffington, 2006; Skeffington *et al.*, 2006a; Skeffington *et al.*, 2006b; Syri *et al.*, 2000; Zak *et al.*, 1997). Recent UK studies e.g. Skeffington *et al.* (2006a) show that uncertainties in critical loads are due mainly to the uncertainties in the individual underlying datasets and the paucity of UK data on which to base model input parameters. Uncertainties in the calculated critical load values are generally less than the uncertainties in individual input parameters; uncertainties can vary from one site to another with no single input parameter being identified as more important than another. Additional site-specific input data for well-studied sites would help reduce the uncertainties. The national maps are based on the best available data and the methods used are consistent with those developed under the Convention on Long-range Transboundary Air Pollution (UNECE, 2004). An analysis of uncertainties in the HARM acid deposition model has been made by Page *et al.* (2008). Using percentiles of HARM-modelled acid deposition for 2005 and 2020 and percentiles of soil acidity critical loads, the potential implications of uncertainties on accumulated exceedance estimations have been considered. The results show that despite uncertainties in both acid deposition and critical loads, a reduction in emissions between 2005 and 2020 produces an accumulated exceedance that is statistically significant from zero at the two standard deviation level. Estimates of reductions in critical load exceedance using FRAME-modelled deposition are also likely to be statistically significant.

5.3 Effects on freshwaters

5.3.1 Introduction

Transboundary air pollutants harm the structure, function and biodiversity of freshwater ecosystems through processes of (i) acidification by compounds of sulphur (S) and nitrogen (N), (ii) eutrophication by N, and (iii) contamination by toxic heavy metals. In the UK, air pollution impacts on freshwater ecology are most obvious in upland lakes and streams remote from intensive agriculture and point source discharges, where organisms are adapted to water of low alkalinity, ionic strength and nutrient concentrations. Pressures tend to be greatest in high rainfall regions close to industrial conurbations where deposition rates are highest, while sensitivity to acidification is highest for waters draining peats, and acid soils overlying lithologies with low weathering rates such as granites, sandstones, greywackes and schists.

Surface waters began to acidify when the deposition of mineral acids outstripped the buffering provided by base cations in catchment soils, resulting in run-off water increasingly enriched with hydrogen and aluminium ions toxic to a range of aquatic fauna at high concentrations. Reduced pH and alkalinity affected the viability of a range of aquatic plants from algae to macrophytes. Compounding direct effects, species losses changed the structure of wider aquatic food webs.

Wide-scale problems in surface waters resulting from ‘acid rain’ were not identified until the 1960s, when the long-range transport of S and N was first linked to a long-term increase in the acidity of precipitation and surface waters and damage to aquatic biota across wide areas of northern Europe (Odén, 1968). Developments in the science of palaeolimnology and palaeoecology (through the study of diatom remains in lake sediment cores) during the 1980s revealed that lakes in the UK were particularly early in showing evidence of acidification, with pH declines beginning as early as the mid-19th century (Battarbee *et al.*, 1990). Acidification has since been shown to have affected lakes and streams in many geologically sensitive areas including Dartmoor, Exmoor, Snowdonia and the Cambrian Mountains of central Wales, the Pennines, the North York Moors, the English Lake District, Galloway, the Trossachs, the Scottish Grampian Mountains and the Mourne Mountains.

Monitoring of the environmental and ecological impacts of acidification in the UK began in the 1980s. The freshwater ecology focus has therefore been on quantifying the efficacy of emissions control on water chemistry and documenting ecological responses. A national programme funded by the Department for Environment, Food and Rural Affairs (Defra), the UK Acid Waters Monitoring Network (AWMN) was established in 1988 (see Figure 5.9) and in recent years has received co-funding and other support from the Scottish Government, the Welsh Assembly Government, the Natural Environment Research Council (NERC) and the Forestry Commission. Other regional- to local-scale monitoring has been conducted by the Fisheries Research Services (FRS) Freshwater Laboratory in Pitlochry (Galloway and Trossachs), Cardiff University (Llyn Brianne catchment), and the Centre for Ecology and Hydrology (CEH) (Plynlimon and the Lake District).

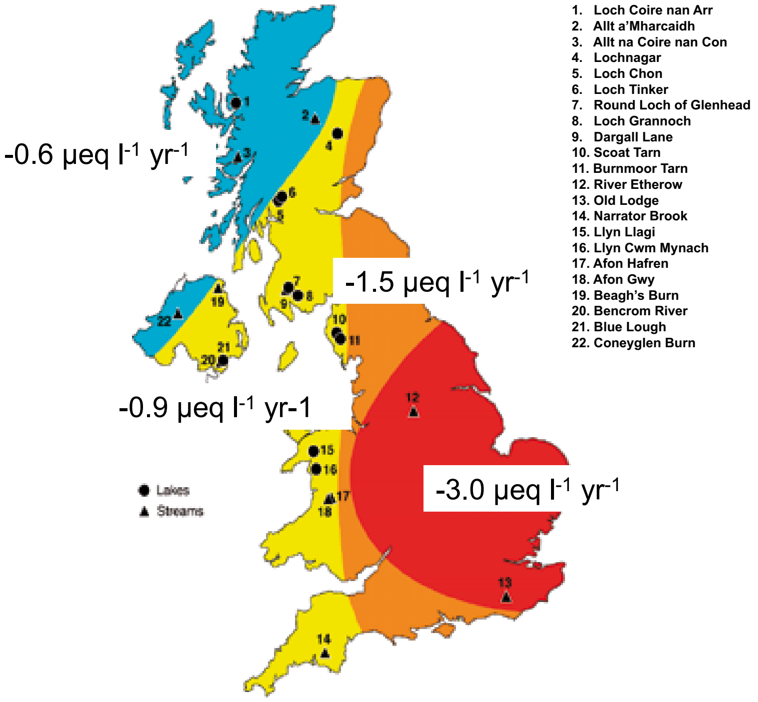

Figure 5.9: Location of key acidification monitoring locations in the UK in relation to the four areas of the UK classified by reductions in rainfall acidity (see Figure 3.21 for more details) (Numbers 1-22 represent AWMN sites (circles = lakes; triangles = streams)).

The effects of deposited N as a nutrient and heavy metals on aquatic ecosystems are less obvious than the effects of acidification. They are not restricted to acid-sensitive waters and are less well-studied. Until recently it was widely assumed that primary productivity in upland waters was limited by phosphorus (P) availability only, but there is increasing evidence that algal composition in these ecosystems is changing in response to atmospheric N deposition. Heavy metals accumulate in aquatic food chains, and certain metals have been reported at levels approaching human health guideline limits in some circumstances (Rippey *et al.*, 2008). As these toxic substances are often derived from similar industrial sources to S and N deposition it can be difficult to distinguish ecological effects from those of acidification, while interactions can occur between metal toxicity and water pH.

In this section we review: (i) evidence that recent reductions in deposition are influencing the chemistry and ecology of acid-sensitive waters; (ii) factors that have confounded expected recovery signals; (iii) evidence of the extent to which freshwater ecosystems may be returning toward their pre-acidification condition; (iv) the importance of N deposition as an agent of eutrophication in upland waters; and (v) the continued gaps in our understanding of how air pollutants threaten aquatic biodiversity, particularly with regard to forecasted future changes in climate. Heavy metal contamination is reviewed in Chapter 6.

5.3.2 Trends in the chemistry of acid-sensitive waters

The main chemical contributors to acid deposition on surface waters are non-marine sulphate (xSO_4^{2-}) and nitrate (NO_3^-) concentrations (i.e. the acid anion drivers), and measures of acidity, i.e. pH, alkalinity and aluminium concentration, that, depending on concentrations of base cations and dissolved organic carbon (DOC), determine biological responses. Acid neutralising capacity (ANC) describes the ability of water to withstand acidification by a strong acid and is determined most simply as the difference between the equivalent concentrations of base cations (calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+) and potassium (K^+)) and acid anions (SO_4^{2-}, NO_3^- and chloride (Cl^-)).

Sulphate

Deposited SO_4^{2-} behaves conservatively within many of the UK's most acidified freshwater catchments. In some conditions SO_4^{2-} ions may be retained by binding to the surfaces of iron and aluminium oxides and hydroxides in the soil, or through bacterial reduction to sulphides in anaerobic conditions in wetlands and lake sediments; however storage capacity in well-drained soil is small relative to inputs. A comparison of estimated depositional fluxes of xSO_4^{2-} to AWMN catchments with estimated run-off (Cooper, 2005), concluded that at most sites xSO_4^{2-} export had kept pace with reduction in xSO_4^{2-} deposition over a period of substantial decline in inputs. Furthermore, unpublished data on SO_4^{2-} adsorption capacity for soils at Plynlimon have confirmed that the sorbed pool is small and unlikely to introduce significant delay in stream water SO_4^{2-} response as deposition declines. As xSO_4^{2-} has been the dominant driver of acidification historically, the absence of significant inertia has encouraging implications for the potential rate of recovery from effects of acid deposition.

Non-marine sulphate concentrations in surface waters across the UK show a coherent pattern of decline over the last two decades. However, Figure 5.10 illustrates differences in concentrations and trend slopes, reflecting geographic gradients in the sulphur deposition loads and trends described in earlier chapters. Proportionally steeper declines in xSO_4^{2-} at the more polluted sites have led to a convergence in concentrations with time (see Table 5.6). The few exceptionally long chemical time series, including FRS records for Galloway and CEH records for the English Lake District, indicate that levels have been falling since at least the late 1970s. After the establishment of the AWMN in the late 1980s concentrations remained relatively stable for almost a decade before falling rapidly between around 1996 and 2000. Since 2000 there is little indication of further reductions at most sites. Concentrations in waters in Galloway now approximate to those recorded for the AWMN 'low deposition control' site, Loch Coire nan Arr, at the onset of monitoring, although even here levels fell significantly in the late 1990s and now average around 5 μeq l^{-1}. Concentrations in most monitored surface waters to the south of Galloway remain at between four times to over an order of magnitude higher than this.

Nitrate

In lake and stream catchments that are not heavily influenced by diffuse or point source domestic, agricultural or industrial contamination, typical of many upland regions in northern Europe, most N is exported in organic form; concentrations of inorganic N (NO_3^- and NH_4^+) are generally very low in comparison, often falling in the range 0-5 μeq l^{-1} (e.g. (Allott *et al.*, 1995; Henriksen *et al.*, 1998)). Where direct catchment sources are absent (intensive agriculture, industrial or urban areas, point sources), elevated NO_3^- concentrations may indicate anthropogenic N deposition. In contrast to deposited S,

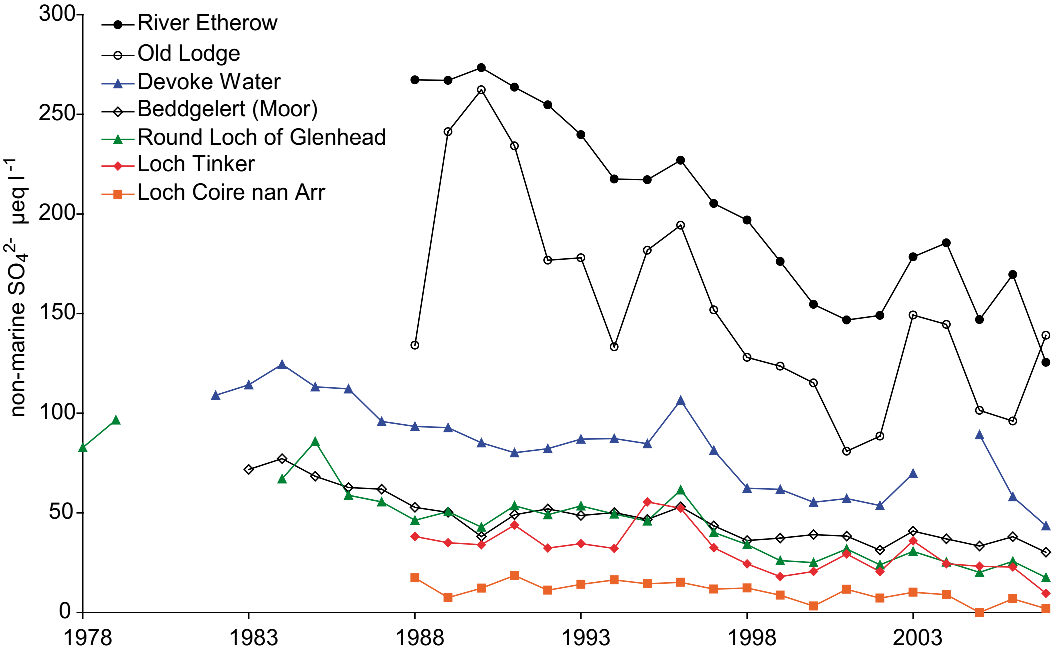

Figure 5.10: Mean annual non-marine sulphate concentrations in a range of UK lakes and streams (Data are provided for: the Round Loch of Glenhead – south-west Scotland (FRS Pitlochry); Devoke Water – English Lake District – and Beddgelert (moorland control site) – North Wales (CEH); Loch Coire Nan Arr – north-west Scotland, Loch Tinker – Trossachs, River Etherow – south Pennines and Old Lodge – south-east England (AWMN).

AWMN site (number)	xSO_4^{2-}	NO_3^-	Cl^-	pH	alkalinity	Lab Al	Ca^{2+}	DOC	ANC
	μeq l^{-1} yr^{-1}	μeq l^{-1} yr^{-1}	μeq l^{-1} yr^{-1}	yr^{-1}	μeq l^{-1} yr^{-1}	μg l^{-1} yr^{-1}	μeq l^{-1} yr^{-1}	mg l^{-1} yr^{-1}	μeq l^{-1} yr^{-1}
Old Lodge (13)	-6.94	0.00	-3.81	0.04	2.27	-3.88	-0.95	0.26	4.63
River Etherow (12)	-6.73	-0.64	-3.19	0.02	2.22	-11.06	-2.69	0.30	4.40
Blue Lough (21)	-2.85	-0.50	-1.81	0.02	0.90	-10.41	-0.95	0.16	2.90
Loch Grannoch (8)	-2.56	-0.07	-2.48	0.01	0.43	-0.27	-1.10	0.19	2.49
Beagh's Burn (19)	-1.60	0.00	-2.23	0.00	0.12	-11.10	-0.70	0.35	2.11
RL Glenhead (7)	-1.58	0.29	-2.09	0.02	0.55	-2.63	-0.40	0.13	1.42
Bencrom River (20)	-1.54	0.14	-1.83	0.04	1.39	-2.92	-0.15	0.09	2.29
Llyn Llagi (15)	-1.35	-0.14	-2.09	0.04	0.57	-0.07	-0.70	0.09	1.11
Loch Tinker (6)	-1.23	0.00	-2.12	0.01	0.24	-1.38	-0.65	0.18	1.23
Loch Chon (5)	-1.21	0.29	-3.75	0.03	1.12	0.00	-0.20	0.20	2.39
Dargall Lane Burn (9)	-1.15	0.00	-1.92	0.03	0.63	-1.18	-0.35	0.08	1.26
Burnmoor Tarn (11)	-1.08	0.00	-3.24	0.01	1.18	-0.58	-1.05	0.10	1.53
Llyn Cwm Mynach (16)	-1.08	0.14	-1.50	0.01	0.19	-0.80	-0.80	0.03	0.38
Lochnagar (4)	-1.00	0.21	-0.87	0.01	0.06	-1.70	-0.40	008	0.41
Coneyglen Burn (22)	-1.00	0.00	0.00	0.00	-0.33	-2.08	-0.05	0.23	0.47
Alit na Coire nan Con (3)	-0.90	0.00	-0.28	0.00	0.00	-2.38	-0.50	0.17	0.90
Afron Hafren (17)	-0.87	-0.14	-1.24	0.02	0.17	0.00	-0.40	0.07	0.59
Afon Gwy (18)	-0.85	0.00	0.00	0.03	0.20	-0.61	-0.10	0.05	0.32
Loch Coire nan Arr	-0.75	0.00	1.41	-0.01	-0.44	0.00	-0.35	0.12	0.25
Scoat Tarn (10)	-0.62	-0.43	-2.37	0.010	0.11	-6.82	-0.65	0.06	1.08
Allt a' Mharcaidh (2)	-0.35	0.00	-0.42	0.00	0.22	-0.2	-0.25	0.08	0.92
Narrator Brook (14)	0.31	0.07	-1.95	0.03	0.62	0.8	-0.15	0.03	0.28

Table 5.6: Trend slopes (Sen's Nonparametric Estimator) for key water chemistry determinands at UK Acid Waters Monitoring Network sites (Figure 5.9) for the period 1988 to March 2008 (Kernan *et al.*, 2010) (lab Al = inorganic monomeric aluminium; DOC = dissolved organic carbon. Site names shaded according to deposition band classification provided in Figure 5.9).

N may be retained significantly by vegetation uptake and microbial processing within catchment soils, particularly in low N deposition regions. Seasonal variation in soil retention of N often results in strong seasonality in surface water NO_3^- concentrations, with peak levels in late winter/early spring and minimum levels in late summer/early autumn. Vulnerability to enhanced NO_3^- leaching has been shown to be linked to catchment characteristics such as soil C and N pools, catchment slope and proportion of bare ground (e.g. Helliwell *et al.*, (2007); Kopácek *et al.*, (2005)).

Stable isotopes in NO_3^- ($^{15}N^{18}O_3^-$) have been used to determine the relative contribution of NO_3^- in run-off from atmospheric deposition versus microbial sources (Campbell *et al.*, 2002; Durka *et al.*, 1994; Spoelstra *et al.*, 2001). Similar studies in the UK uplands suggest that at least 70% of leached NO_3^- has been microbially cycled (Curtis and Simpson, 2007). Surface water NO_3^- may therefore originate in deposition as nitrogen oxides (NO_x) or reduced N, but in both cases, and explicit in the definition of ANC, leached NO_3^- in these catchments represents a net contribution to the acidity of the receiving surface water.

Nitrate concentrations in acid-sensitive lakes in many regions increased from low levels during the 1970s and 1980s (e.g. (Brown, 1988; Grennfelt and Hultberg, 1986;

Henriksen and Brakke, 1988) (Figure 5.11) in an apparent response to increased N deposition. Later studies confirmed that NO_3^- had become a contributor to acidification in many parts of Europe and North America (e.g. (Allott *et al.*, 1995; Henriksen *et al.*, 1997; Murdoch and Stoddard, 1992; Stoddard, 1994; Wright *et al.*, 2001).

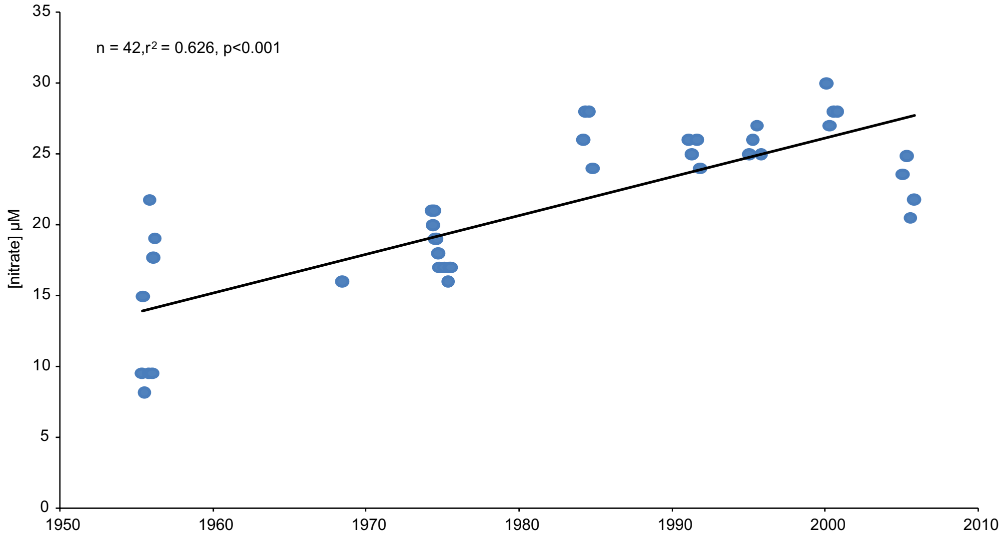

Figure 5.11: Nitrate concentration in occasional samples from the outflow from Wastwater, English Lake District (CEH).

Empirical data from forested (Dise and Wright, 1995; Gundersen *et al.*, 1998) and moorland (Curtis and Simpson, 2007) ecosystems in Europe show clear relationships between N deposition and N export. Nitrate leaching is normally undetectable throughout most of the year and concentrations very rarely rise above 5 µeq l^{-1} when N deposition levels remain below 9 kg N ha^{-1} yr^{1}, but is sustained at higher concentrations when deposition exceeds 25 kg N $ha^{-1}yr^{1}$. However, nitrogen saturation theory (Aber *et al.*, 1989; Stoddard, 1994) suggests that NO_3^- levels could continue to rise even under constant or declining N deposition loads. Terrestrial accumulation of N should raise the N content of vegetation and soils and reduce carbon:nitrogen (C:N) ratios in soil organic matter, potentially increasing nitrification rates and nitrate leaching (Dise and Wright, 1995; Gundersen *et al.*, 1998). A simple mass-balance model for N, the First-order Acidity Balance (FAB) model (Posch *et al.*, 1997), that uses best available estimates of long-term steady-state sinks for N deposition (Curtis *et al.*, 1998; Curtis *et al.*, 2005b) predicts future NO_3^- fluxes much greater than current observations. Long-term observations and dynamic model simulations suggest that N saturation could be a very slow process (Evans *et al.*, 2006a; Wright *et al.*, 2001).

Stoddard (1994) categorised catchments into four N ‘saturation’ classes, ranging from Stage 0 (where NO_3^- is undetectable in surface water throughout the year) to Stage 3 (where NO_3^- concentrations are continuously high, with no significant seasonal depletion). All four stages are represented by AWMN sites, and they show an increasing contribution of NO_3^- relative to total nitrogen (TN) in successive stages. Saturation stage, and the contribution of NO_3^- to TN, is clearly linked to N deposition levels, illustrating the importance of N deposition as an acidifying agent in these systems (Figure 5.12).

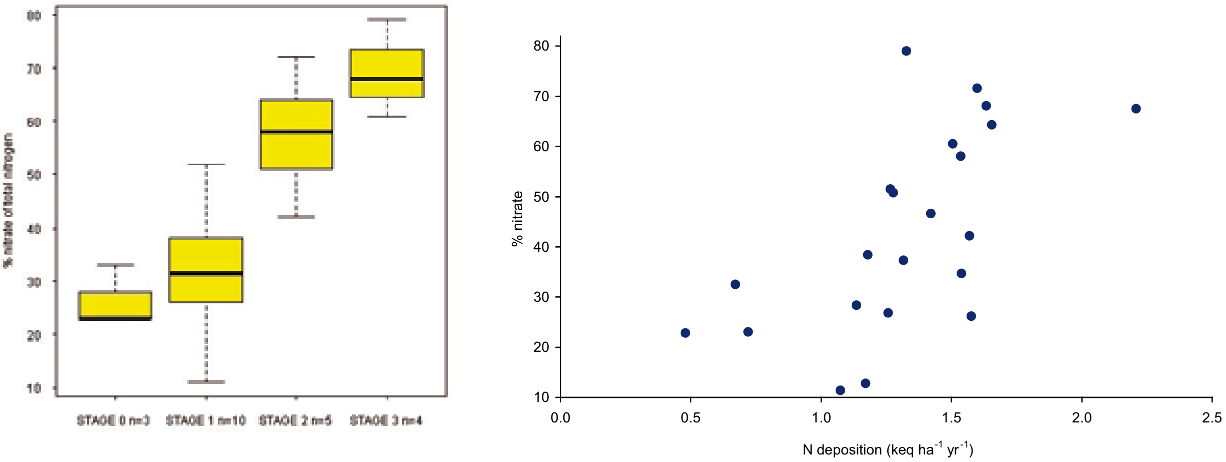

Figure 5.12: Mean percentage contribution of nitrate to total nitrogen concentration in relation to (a) the Stoddard (1994) saturation stages: Stage 0 = almost complete N retention; STAGE 1 = seasonal (spring) leaching of nitrate only; STAGE 2 = year round nitrate leaching but with some seasonality; STAGE 3 = year round leaching at high levels and little seasonal pattern and (b) estimated N deposition for 22 AWMN sites. Source AWMN.

Few monitoring records, however, are of sufficient length to illustrate the N saturation process. Long-term changes in NO_3^- concentrations are confused by substantial diurnal and seasonal variability (e.g. (Reynolds and Edwards, 1995) and decadal level variability linked to the North Atlantic Oscillation (Monteith *et al.*, 2000). The absence of a clear trend in recent years at a European scale has been suggested to result from opposing factors, i.e. the increasing N saturation status of catchments against a background of declining N deposition in some parts of Europe (Wright *et al.*, 2001). In the UK, soil C:N ratios in isolation are not sufficient to explain surface water NO_3^- concentrations or the proportion of total N deposition leached as NO_3^- (Curtis and Simpson, 2007; Curtis *et al.*, 2004). It is possible that soil disturbance during moorland management, e.g. by burning or peat erosion, may have confounded N deposition inventories (Cresser *et al.*, 2004), but vegetation type (Rowe *et al.*, 2006) and the density of bryophyte and lichen cover (Curtis and Simpson, 2007; Curtis *et al.*, 2005a) may also have an important influence on N assimilation and interception rates.

Direct links between N deposition, soil C:N ratio and a nitrification 'switch' that increases NO_3^- leaching have not been convincingly demonstrated in the UK uplands. Nitrate concentrations have increased significantly at two Scottish AWMN sites over the past 20 years (Table 5.6; Figure 5.13), and an increase in NO_3^- over the first 15 years of monitoring at Lochnagar was sufficient to negate the effect of the reduction in SO_4^{2-} on lake water ANC. However, even over this timescale it is difficult to rule out the influence of climatic variability, and concentrations at Lochnagar have fallen more recently. Even where NO_3^- concentrations have remained level, the case for the majority of AWMN sites, the relative role of NO_3^- in residual acidification is increasing as

SO_4^{2-} concentrations continue to fall in response to declining S emissions (Curtis *et al.*, 2005b).

Acidity

Acid deposition in excess of soil buffering capacity results in reductions in alkalinity and pH and an increase in the availability of inorganic aluminium (Al_i). The net effect is summarised by the level of reduction in ANC, the physico-chemical parameter most readily computed by process-based acidification models such as MAGIC (see Chapter 4). ANC also has biological relevance. Lien *et al.* (1996) showed that 95% of lakes in a Norwegian study with an ANC greater than 20 μeq l^{-1} (subsequently adopted as a biological 'critical limit') showed no long-term decline in their brown trout populations, 50% of lakes with an ANC of zero had reduced populations, while all fish were extinct in lakes with ANC levels below -40 μeq l^{-1}. The physiological explanation for the relationship may lie in the steep gradients in labile Al mobilisation at around these ANC levels and the rapid change in pH that occurs between 0 to 20 μeq l^{-1} ANC. Subsequent work has shown that biological sensitivity to ANC depends on the relative contribution of dissolved organic carbon (DOC) to the ionic balance (Lydersen *et al.*, 2004; McCartney *et al.*, 2003), and considerably higher levels of ANC (around 40-50 μeq l^{-1}) may be necessary to protect some sensitive species when DOC is high. Furthermore, episodic depression of ANC during periods of high flow, or after sea-salt deposition events, can result in damage to the health or even loss of aquatic organisms – with sensitivity often varying over the course of the life cycle, so average ANC levels may not

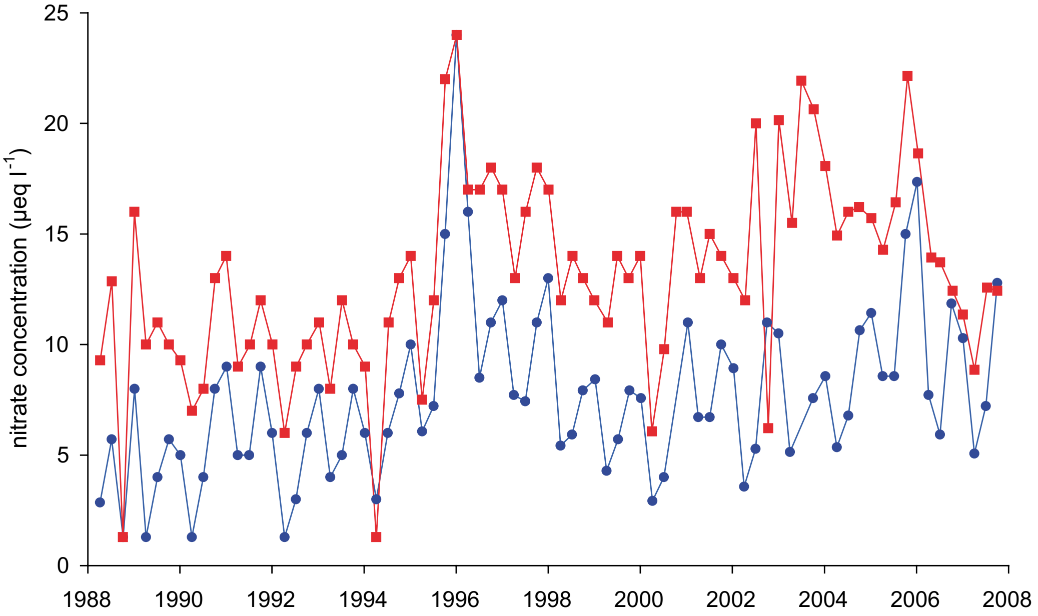

Figure 5.13: Time series of nitrate concentrations (μeq l^{-1}) at the two AWMN sites to show statistically significant upwards trends over the last two decades. Blue circles = Round Loch of Glenhead (a moorland site in Galloway); red squares = Loch Chon (a partly forested site in the Trossachs). Source AWMN.

necessarily provide the best guide for ecological protection. AWMN data show a clear increase in ANC at almost all sites over the last two decades. These are proportional to reductions in acid anion inputs (i.e. xSO_4^{2-} reductions), although a long-term reduction in sea-salt deposition, and at some sites in non-marine Cl^-, also contribute to this improvement (Table 5.6; Figure 5.14).

Stoichiometrically, ANC increases are accounted for largely by falling H^+ (i.e. rising pH) and inorganic Al (Al_i) concentrations, but also by a rise in DOC concentration (Table 5.6; Section 5.3.2). At the more acidic sites, reductions in Al_i are particularly pronounced (Figure 5.15) and, importantly, the largest reductions are seen at the height of episodic maxima (generated at times of high flow or sea-salt events – Section 5.3.2) that in association with pH minima may impose a ceiling for biological recovery (Lepori *et al.*, 2003). However, it is important to note that contemporary Al_i concentrations at these sites are still high – sensitive waters in regions with historically low levels of S deposition rarely show concentrations above 10 μg l^{-1} – and may continue to be toxic, at least episodically, to sensitive biota.

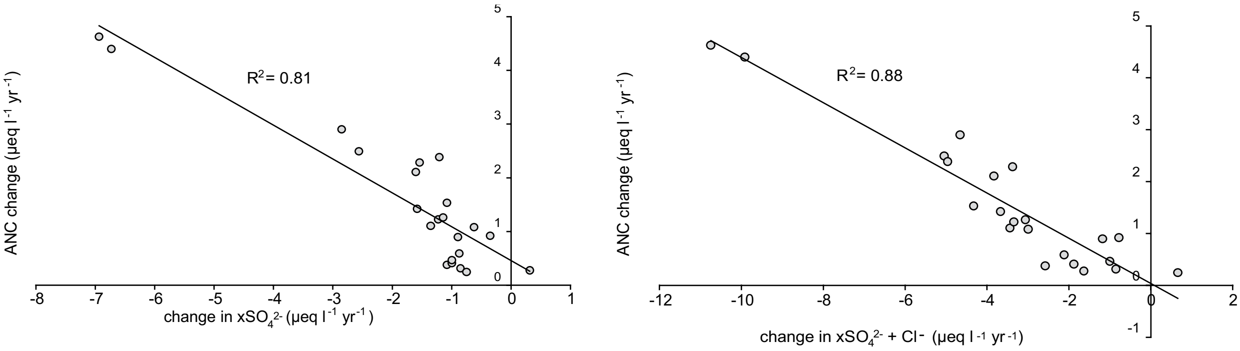

Figure 5.14: Relationship between (a) the rate of change in ANC and the rate of change in xSO_4^{2-} and (b) the net rate of change in xSO_4^{2-} and Cl^- at the 22 AWMN sites (Based on data provided in Table 5.6).

The relative response of Al_i, pH or bicarbonate alkalinity to changing ANC is dependent on the point on the ANC gradient and amount of buffering provided by DOC. pH changes sigmoidally with ANC, with the sharpest change occurring between around 0-20 μeq l^{-1} ANC (Figure 5.16), and is steepest for sites with low DOC concentrations. This is important for several of the more acidified AWMN sites, and recovering acidified lakes and streams more generally, as their current average ANC often falls within this range. For these sites, further reductions in the acid load should result in disproportionately rapid improvements in pH. As pH is considered a 'master variable' with respect to ecological response (Petchy *et al.*, 2004), many of the UK's more acidified aquatic ecosystems could currently be considered at a critical phase in their recovery for this reason.

At the forested sites, Loch Grannoch, Afon Hafren and Llyn Cwm Mynach, most of the reduction in xSO_4^{2-} to date has been accompanied by a decrease in Al_i (Table 5.6; Section 5.3.2). At the other end of the acidity gradient, there has been no change in pH in the

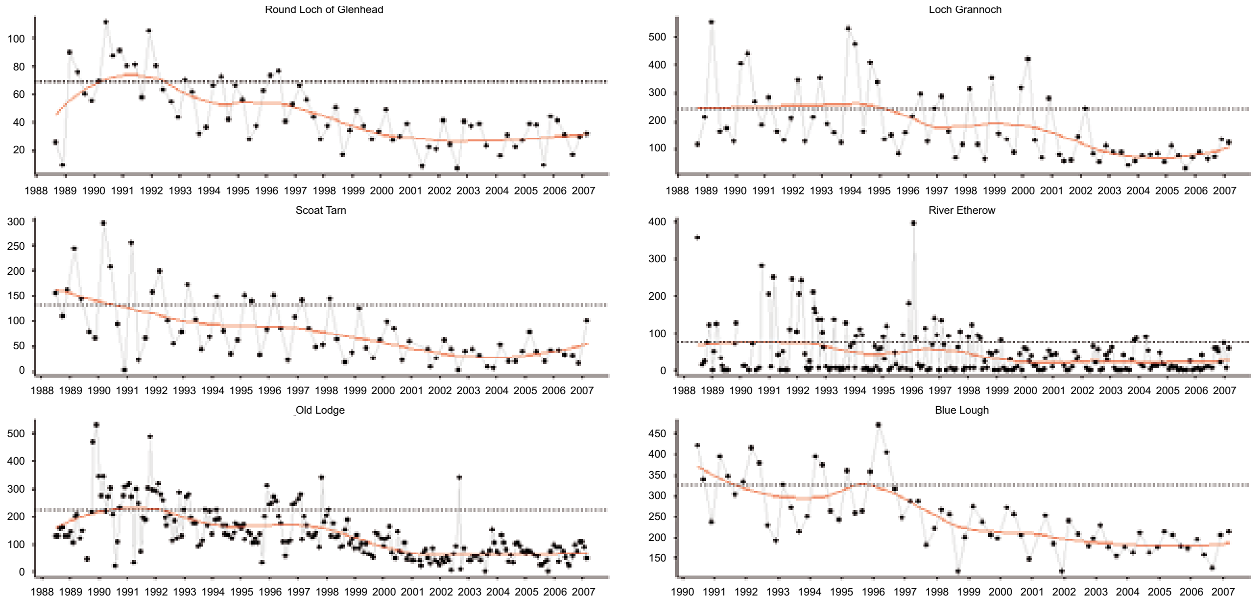

Figure 5.15: Time series (1988-2007) of inorganic (labile) aluminium concentrations (µg l^{-1}) at six of the most acidic AWMN sites (Red line = lowess smoother; dotted line = 1988-93 mean). Source AWMN.

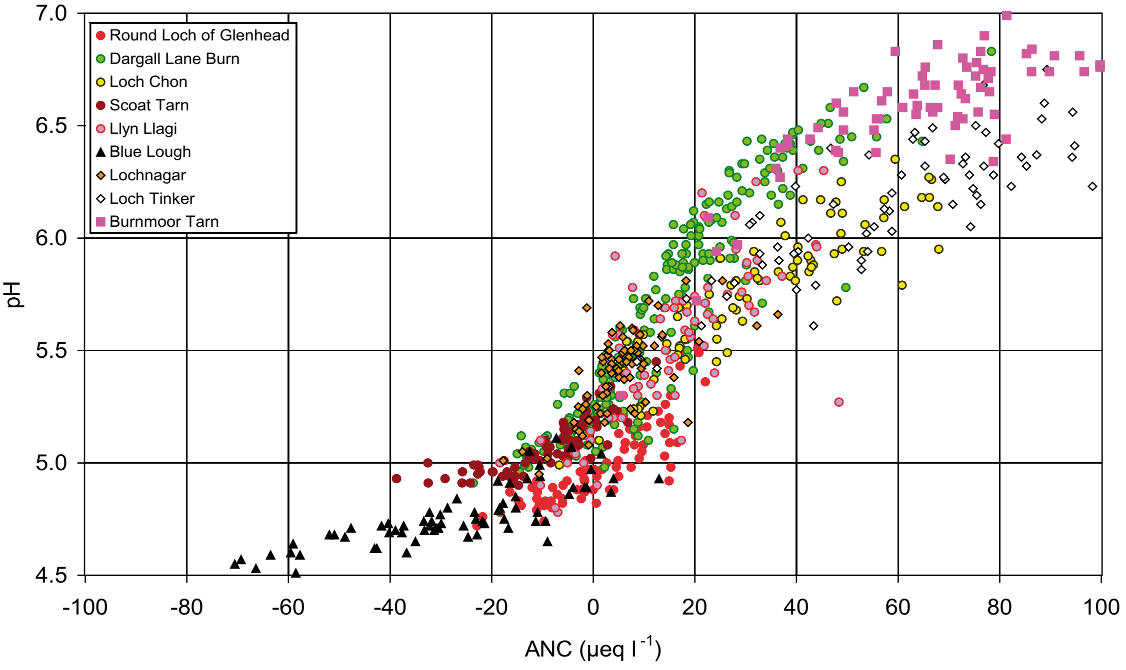

Figure 5.16: Relationship between pH and ANC for individual water samples for a range of AWMN sites (1988-2008) (Note the relatively steep slope between 0-20 µeq l^{-1} ANC; as ANC at all sites is increasing, points to the extreme right of each time series generally represent the most recent data.) Source AWMN.

relatively well buffered Burnmoor Tarn (mean 6.5), but bicarbonate alkalinity has risen significantly.

Rising levels of dissolved organic carbon

Dissolved organic carbon (DOC) in more remote surface waters comprises a range of organic compounds, but is often dominated by humic and fulvic acids, largely derived from the decomposition of soil organic matter, that reduce water transparency and contribute acidity. One of the unexpected results from the AWMN chemical monitoring programme was the first identification of a substantial regional rise in DOC concentrations (Freeman *et al.*, 2001) (see Figure 5.17), a finding since reported for several other acidification monitoring networks (e.g. (Skjelkvåle *et al.*, 2005).

A causal relationship between acidification and a reduction in DOC leaching was suggested in the 1980s (Krug and Frink, 1983; Tipping and Hurley, 1988), but rising trends observed across the AWMN were initially believed to result from climatic factors such as soil warming (e.g. (NEGTAP, 2001). With longer datasets and further research, a large part of the observed increases have now been shown to be due to recovery from acidification, both in the UK (Evans *et al.*, 2006b) and internationally (Monteith *et al.*, 2007). In the UK DOC concentrations have increased in proportion to reductions in the deposition of both SO_4^{2-} and Cl^- over the last two decades, and the response is sharper for waters with lower base cation concentrations.

While the mechanism driving the DOC response to decreasing acid deposition is still under investigation, it is clear that the recent rising concentration of organic acids has offset some

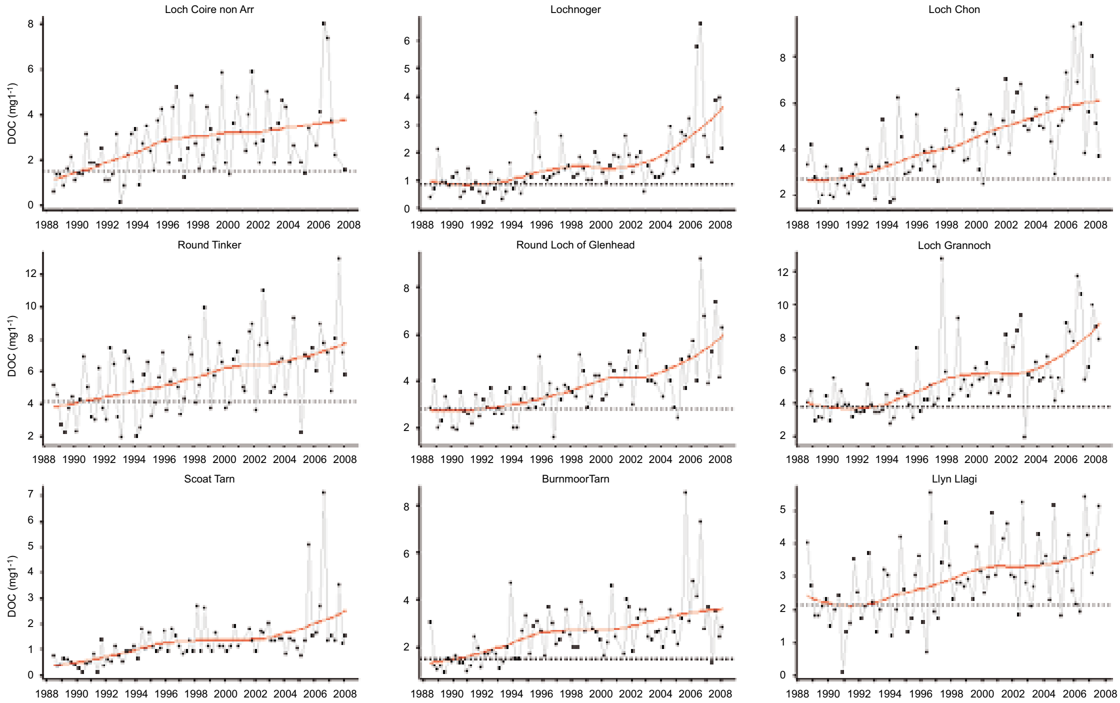

Figure 5.17: Time series (1988-2008) of dissolved organic carbon concentrations (mg l^{-1}) in nine AWMN lakes. Red line = lowess smoother; dotted line = 1988-93 mean. Source AWMN.

of the potential benefits of a decline in SO_4^{2-}, as the response of acidity to falling levels of deposition has been smaller than expected. An assessment of ionic changes across the UK AWMN from 1988-2003 by Evans *et al.* (2008b) provides an indication of the scale of this effect (Figure 5.18). While complicated by concurrent changes in sea-salt deposition and variation between sites, on average 33% of the decline in acidity resulting from the decrease in xSO_4^{2-} has been offset by an increase in organic acidity. Similar values have been observed in North America (36%; (Driscoll *et al.*, 2003)) and Sweden (29%; (Erlandsson *et al.*, 2010)). This organic acid buffering is of similar scale to (well-quantified) buffering by base cations, such that only around 25% of the reduction in xSO_4^{2-} has translated into decreases in H^+ or Al_i, or increases in bicarbonate (HCO_3^-). If, as has been suggested, increases in DOC are directly linked to soil acidity, then the role of organic acids as a buffer should be considered an integral component of the recovery process. One implication of these observations is that the 'reference' pH of many acidified surface waters may be lower than estimated by models that have assumed DOC concentrations have remained constant, and may account for discrepancies between process-based and diatom-based estimates (Battarbee *et al.*, 2005).

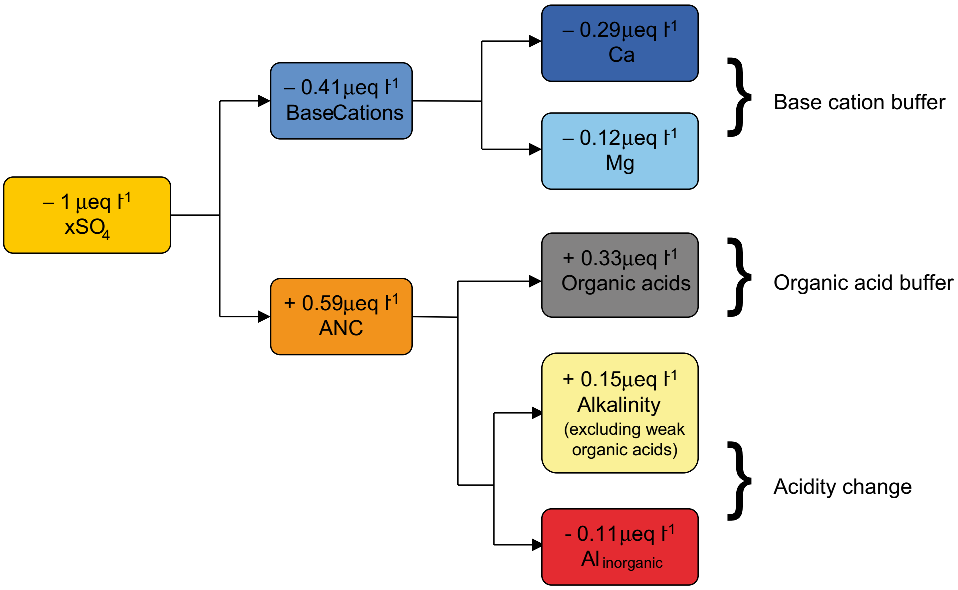

Figure 5.18: Average response of UK AWMN surface waters per 1 µeq l^{-1} decrease in non-marine sulphate concentrations (Evans *et al*., 2008a). Assuming that changes in marine anion deposition have been entirely balanced by changes in marine base cations; +/- symbols indicate increase/decrease respectively.

5.3.3 Dynamic modelling of chemical recovery

The response of soils and freshwaters to changes in the chemical climate clearly has a dynamic component due to chemical interactions between the soil water and solid phase components which operate on a range of timescales. Modelled changes in soil and freshwater chemistry in response to changing wet- and dry-deposited pollutants have formed an important component of the synthesis of the long-term trends in acidification. As this includes interpretation of the responses to reductions in deposition, this research is presented in Chapter 8, Recovery (Section 8.5).

5.3.4 Ecological responses to reductions in acidity

Acidification has resulted in widespread damage to aquatic biodiversity through the loss of acid-sensitive species at all trophic levels from primary producers (i.e. aquatic plants) to top predators including fish and riverine birds. Toxicological effects are wide-ranging, but for fish include the disruptive effects of high concentrations of aluminium and hydrogen ions on egg production, hatching success, osmo-regulation and gill function, (Booth *et al.*, 1988; Donaghy and Verspoor, 1997; Kroglund *et al.*, 2008). Damage to salmonid stocks particularly was a major driver of international emissions control enacted through the UNECE LRTAP Convention. Thorough monitoring of aquatic ecosystems is essential to assess the extent to which international action on emissions is achieving, and will continue to achieve, its intended effect. The UK AWMN currently provides 20-year records of diatom, aquatic macrophyte and macroinvertebrate populations for the majority of its sites, while monitoring of salmonids has been scaled back to eight sites since 2006 due to cuts in funding. In addition to their contribution to the AWMN, Marine Scotland Pitlochry continues to monitor salmonid populations at other acidified sites in Scotland, while Cardiff University has maintained a 28-year invertebrate monitoring record of the effects of deposition reductions, climate and experimental liming in the Llyn Brianne catchment.

In the 20-year AWMN interpretive assessment covering the period 1988-2008 (Kernan *et al.*, 2010) evidence for ecological change consistent with reductions in water acidity is shown to be widespread and more extensive than reported by Monteith *et al.* (2005). All lakes and five streams now show significant trends in diatom species composition, and these are indicative of declining levels of acidity. At some sites, such as Llyn Llagi (Snowdonia), there has been a substantial decrease in the relative abundance of diatom species shown from palaeoecological evidence to have been very rare prior to acidification but having become dominant during the acidification phase. Aquatic macrophytes with elodeid (i.e. branching) growth forms, that obtain dissolved inorganic carbon from the water column (rather than from sediments), have been recorded for the first time recently in several AWMN lakes, and acid-sensitive mosses have been detected recently in some recovering streams. Significant changes in macroinvertebrate communities are now reported for 16 out of 22 AWMN sites. These involve mostly very small changes in the relative abundance of species, but are often characterised by the recent appearance and/or an increase in proportion of predatory species, including net spinning caddis in several lakes and predatory stonefly and mayfly in some streams. Changes in lake and stream communities often result in changes in macroinvertebrate acidification indicator scores indicative of recovery responses, although the communities of the more acidic lakes tend to show the least evidence of improvement and scores remain considerably below those of assumed 'reference' communities.

AWMN fish data when amalgamated for all sites show a clear positive relationship between brown trout density and ANC (Monteith *et al.*, 2005), although few sites currently show significant long-term trends of rising densities despite improvements in ANC; substantial short-term variability in densities, possibly dominated by physical conditions and acid episodicity at the time of sampling, dominated at most sites. However, at three of the most acidic sites on the AWMN, Old Lodge (Figure 5.19), Scoat Tarn and Blue Lough, small numbers of brown trout fry were recorded only recently for the first time since monitoring began. While biological changes are widespread across the AWMN and generally consistent with falling levels of acidity, the degree of change is often smaller than had been anticipated and communities are not always returning towards reference assemblages (Section 5.3.6).

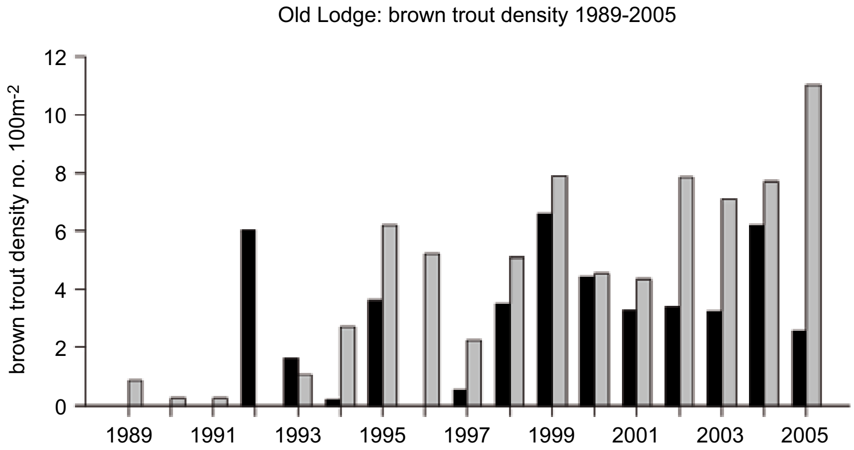

Figure 5.19: Densities of brown trout in the chemically recovering AWMN stream Old Lodge. Black bars = fry; grey bars = fish >1 year old. Source AWMN.

Data collected from the experimental catchments at Llyn Brianne over the last 25 years allow a comparison of ecological recovery between acid moorland, acid forest and circumneutral control streams, while experimental additions of calcium carbonate, funded by Defra in 1987/88, illustrate how induced recovery and 'natural' recovery have progressed (Ormerod and Durance, 2009). Mean H^+ concentrations in acid moorland streams have fallen by around 15-16 µeq l^{-1} over the last 25 years, increasing mean winter pH by 0.8-1.3 units to pH 5.6-6.1. Liming moorland streams in 1987/88 increased mean pH to 5.5-6.4, but differences from naturally recovering streams diminished over 12-18 years. In limed and acid moorland streams, changes among invertebrates have been consistent with recovery, and near-identical. However, the extent of change – four acid-sensitive species have increased significantly in abundance or occurrence from a local pool of 29 acid-sensitive species – has been insufficient for any increase in similarity with adjacent circumneutral reference streams (Figure 5.20).

Among possible limits on rates of macroinvertebrate recovery in these streams, multiple lines of evidence suggest that continued episodic acidification during high-flow events is the most important (Kowalik *et al.*, 2007; Kowalik and Ormerod, 2006). Acid episodes still occur widely in acid-sensitive areas, although again pH minima have increased through time. Climate plays a critical role in recovery rate and, after accounting for long-term trends, wet winters and associated episodes increased acidity in moorland and forest streams sufficiently at Llyn Brianne to offset about 20-40% of the total 25-year decrease in H^+ concentration (Table 5.6). Warmer, wetter winters also reduce stability from year-to-year in invertebrate species composition (Bradley and Ormerod, 2001).

Other explanations are necessary to explain the apparently muted nature of macroinvertebrate recovery in most AWMN lakes that are physically better buffered against episodic effects than most streams. In some systems elevated Al_i concentrations may continue to represent a barrier to the return of some sensitive species, while the contemporary biological community itself may impose limits on biological recovery. For example, Ledger and Hildrew (2005) proposed that acid-tolerant generalist species may have filled the algal grazing niche, and may be preventing more acid-sensitive grazers from re-establishing as water chemistry improves. The suggestion that recovery of macroinvertebrates may be restricted by limitations on dispersal were not supported by Masters *et al*. (2007), who reported repeated visits by the adults of sensitive nymphs to the banks of affected streams but no evidence of successful recolonisation.

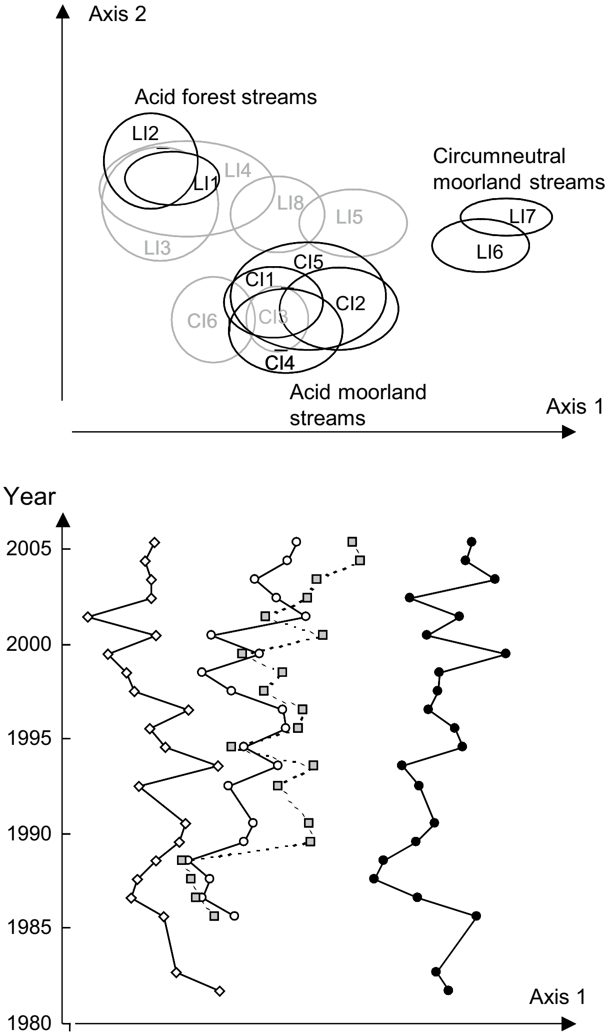

Figure 5.20: The ordination of macroinvertebrates in 14 streams at Llyn Brianne over the period 1981-2005, and the trends in assemblages revealed by the resulting major axis (In the top panel, the positions occupied by each stream through time are indicated by ellipses, while the lower panel plots the changing position of replicate pairs of circumneutral streams (LI6, LI7•), acid moorland streams (CI4, CI1 ○), limed moorland streams (CI5, CI2 ▪), and acid forest streams (LI1, LI2 ◇). Movement towards the right indicates recovery or non-acid conditions; (Ormerod and Durance, 2009)).

5.3.5 The confounding influence of acid episodes

The long-term consequence of future changes in climate for the recovery of acidified waters from acidification is considered together with soils and vegetation in Section 5.5.3. Here we consider the importance of extreme events, in the form of acidic episodes, that are most pertinent for surface waters and particularly streams. Although most surface waters are now recovering from acidification, many remain susceptible to acid episodes, due to the legacy of base cation depletion and pollutant accumulation in soils. Acid episodes are invariably associated with climatic extremes, i.e. high flow, sea-salt events, freeze-thaw and drought; any increase in their frequency and/or intensity would raise the risk of biologically harmful events, and pose a barrier to biological recovery.

High flow events

High flows, triggered by rain or snowmelt, increase flow through upper organic soil horizons, leading to episodic run-off acidification through base cation dilution and increased DOC leaching. A rising incidence of extreme rainfall events might therefore be expected to lead to more severe acid episodes. However, analyses of Plynlimon stream chemistry data (Figure 5.21) suggest that (a) episodic extremes in acidity and aluminium have declined progressively in response to falling deposition, and (b) at very high flows, stream chemistry is relatively insensitive to further change. Evans *et al*. (2008b) therefore concluded that, although high flows will continue to be associated with acidic conditions, climate change-induced increases in discharge maxima are unlikely to offset substantially the benefits of reduced acid deposition.

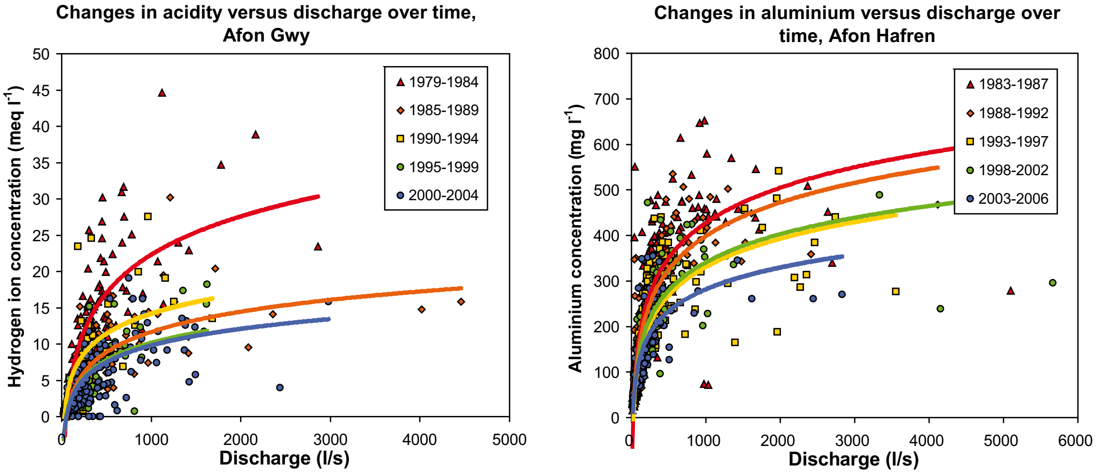

Figure 5.21: Changing relationship between stream discharge and hydrogen ion concentration (Gwy) and aluminium concentration (Hafren) during different monitoring periods (Logarithmic best fit lines shown for each time period. Source CEH.

Sea-salt events

Sea-salt deposition events, associated with periods of strong westerly air flow, were identified in the NEGTAP (2001) report as a major driver of acid episodes in coastal regions. The severity of sea-salt acidification is intensified by anthropogenic acidification, as marine base cation deposition leads to displacement of H^+ and Al_i (rather than non-marine base cations) from soil exchange sites to the stream. Models (e.g. Evans, (2005) suggest that previously acidified catchments will remain sensitive to sea-salt acidification for many decades, as a consequence of the slow recovery in soil base status. Climate change could lead to more severe sea-salt deposition events (UKCIP, 2002), causing repeated setbacks in the recovery of ANC and acid-sensitive biota in acidified systems in the west of the UK. However, the period of enhanced sea-salt deposition observed in the UK in the early 1990s, associated with unprecedented high values of the winter North Atlantic Oscillation Index, has so far not recurred and the overall 20-year trend at most AWMN sites has been downward (Kernan *et al.*, 2010).

Freeze-thaw events

Soil freezing has been linked to pulses of NO_3^- leaching in many experimental and monitoring studies (e.g. (Matzner and Borken, 2008; Mitchell *et al.*, 1996; Monteith *et al.*, 2000). Long-term accumulation of N in catchment soils may increase surface water susceptibility to acidic NO_3^- pulses, but this may be offset by a reduced frequency and severity of winter freezing events under climate change.

Drought-rewet events

Although the retention of deposited S by catchment soils does not appear to be a major factor at the majority of UK monitoring sites, retention in anaerobic peat soils may have significantly reduced the severity of freshwater acidification in more peaty catchments. However, the accumulated S may be susceptible to remobilisation under climate change. Re-oxidation of S to SO_4^{2-} as peats become aerobic during droughts has been shown to trigger severe acid pulses in subsequent rain events (e.g. (Adamson *et al.*, 2001; Bottrell *et al.*, 2004; Hughes *et al.*, 1997). If droughts become more frequent or extreme in future, these acid pulses could severely retard chemical and biological recovery. An exacerbating factor could be increased peat erosion (also potentially a consequence of climate change), with gullying leading to water table drawdown, and exposure of a greater proportion of the historic S store to re-oxidation and export (Daniels *et al.*, 2008).

5.3.6 Progress to 'good ecological status'

The Water Framework Directive (WFD) aims to provide comprehensive management of inland surface, estuarine and coastal waters and groundwater across the European Community, using a common approach with regard to objectives, principles and basic measures. Its fundamental objective is to maintain 'high status' of waters where it exists, prevent deterioration in the existing status of waters and achieve at least 'good status' in relation to all waters by 2015. A key difference between the WFD and previous EU water legislation is its focus on setting ecological (rather than simply water quality) objectives in order to protect and/or restore the structure and function of aquatic ecosystems, and in so doing safeguard the sustainable use of water resources. Another important difference is the emphasis on the development of River Basin Management Plans (RBMPs) as a basis for local management of pressures.

The UK Technical Advisory Group (UKTAG) has the responsibility for setting physico-chemical standards for pressures and developing biological tools for ecological assessment. While the purpose of the WFD is to establish a framework for the protection of all waters, one area of concern with respect to effects of acidification is that many sensitive headwater streams and lakes are not designated as ‘separate water bodies’ by UKTAG on the grounds that catchment areas or lake areas fall under 10 km^2 or 0.5 km^2 respectively. As such they are not considered under the RBMPs and have not been selected for routine WFD monitoring by the national environmental agencies. Most AWMN sites and a substantial proportion of FAB sites (Section 5.3.2) fall beneath these size thresholds, and the process by which these sites, often the most vulnerable to acidification, will be afforded protection under the WFD remains to be clarified.

Most AWMN forested sites are heavily acidified (i.e. Afon Hafren, Llyn Cwm Mynach and Loch Grannoch). They show increases in ANC that are proportionate to reductions in acid deposition but this is manifested mainly by decreases in Al_i which remain at potentially toxic concentrations and there is relatively little evidence of pH increase or biological recovery to date. Tools are being developed to assess ecological status according to WFD ‘Normative Definitions’ based on taxonomic composition and abundance, the ratio of disturbance-sensitive taxa to insensitive taxa, the presence/absence of major taxonomic groups, and levels of diversity. Currently there are discrepancies between UKTAG acidification water quality standards for still and flowing waters. ANC has been proposed as the physico-chemical acidification standard for lakes (>40 $\mu eq\ l^{-1}$ = High; 20-40 $\mu eq\ l^{-1}$ = Good) and it is likely that a comparable system will eventually be adopted for streams.

Palaeoecological data from AWMN lakes provide an opportunity to place recent ecological change in a much longer-term historical context. In 1991 sediment traps were installed in each lake in order to catch diatoms sedimenting to the lake bottom. By combining the data from the traps with the diatom data from sediment cores it has been possible to track changes in the diatom flora of each site continuously from 1800 AD, representing pre-acidification reference conditions, through to the present day using a standard approach. These unique time series (see for example that for the Round Loch of Glenhead in Figure 5.22) enable the response of the lake diatom assemblages to reduced acid deposition to be compared directly with the reference assemblages (represented by the pre-1850 sediments) and with the assemblages that characterised the lakes at the time of maximum acidity.

The results show no evidence for recovery from acidification for two lakes, Lyn Cwm Mynach and Loch Grannoch, both of which have catchments dominated by plantation forestry. Of the remaining nine sites, some show clear evidence for the species composition to be heading back in the direction of the reference assemblage (cf. Figure 5.19), but for the majority of sites contemporary diatom assemblages remain very different from reference and indicate considerably lower pH, whereas for others the ‘recovery’ trajectory is deflected away from the reference direction. Differences between contemporary and reference diatom inferred pH may in part reflect the current stage in chemical recovery at more acidified sites (as suggested in Figure 5.16). The reason for the deflection is not yet clear but work is progressing to evaluate whether changes in assemblage composition are due to: (i) stochastic processes; (ii) hysteresis related to internal ecological processes; or (iii) external factors including the influence of increased nutrient N deposition or climate change and/or their interaction. The last explanation is thought to be the most likely as NO_3^- concentrations remain relatively high at most sites and surface water temperatures are likely to have been increasing in recent decades in line with rising air temperatures. Overall the data show a positive response to the observed decrease in acid deposition but the extent of the recovery is limited.

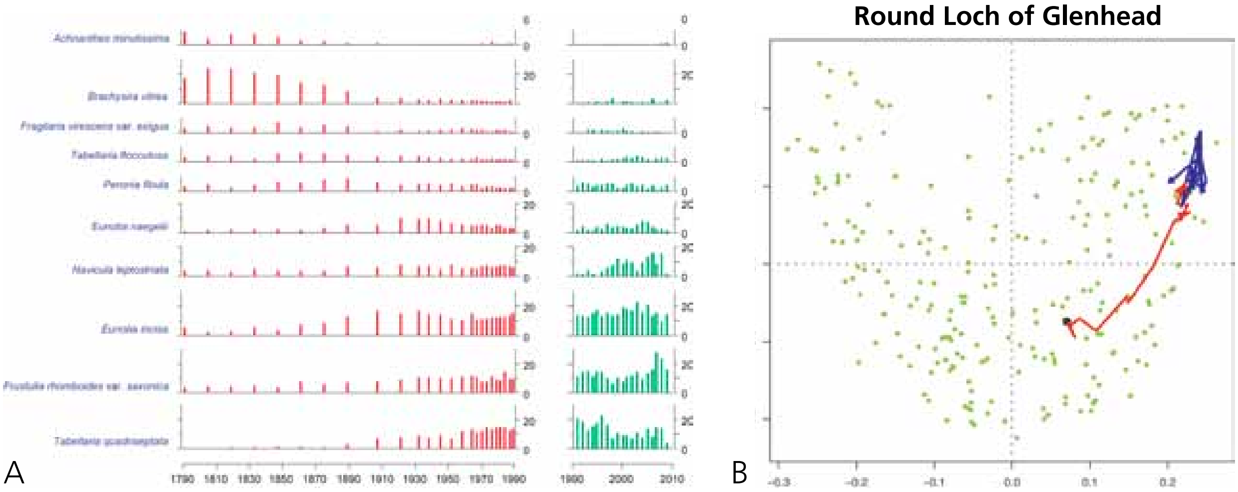

Figure 5.22: (a) Sediment diatom relative abundance (% of all taxa) in a ^{210}Pb dated sediment core taken in 1990 and annually retrieved sediment traps retrieved since 1991; (b) Principal Components Analysis plot of samples in Figure 5.22a in an ordination of surface sediment samples from 138 lakes included in the Surface Waters Acidification Project. Black dot represents position of 1850 sediment core sample; red line represents trajectory to core top (1990) and subsequent sediment trap samples (blue line). Source Environmental Change Research Centre, UCL.

5.3.7 Trends in exceedance of critical loads for acidity

Critical load exceedance maps (Figure 5.23) provide a snapshot of the acidification status of 1752 acid-sensitive waters across the UK, based on the application of the FAB model (Henriksen and Posch, 2001). The model uses single water chemistry samples, CBED (or FRAME) deposition estimates, and, for most sites, an ANC critical limit of 20 μeq l^{-1} (47 sites have an ANC limit of 0 μeq l^{-1}). The maps indicate substantial reductions in levels of exceedance from 1986-88 to 2006-08, particularly with respect to mid- and north Wales, the southern Pennines, the English Lake District and Galloway. Table 5.7 suggests that there has been a particularly strong reduction in the number of FAB sites exceeded in Wales and Scotland, whereas English sites, dominated by areas of relatively high deposition such as the southern Pennines and the North York Moors, show the least reduction. On the basis of future deposition predicted by FRAME, 49% of all FAB sites in England (n = 425) will still be exceeded in 2020 – a reduction of 19% from 1986-88 levels; a substantial proportion of sites in the southern Pennines and the North York Moors will continue to be exceeded by 1-2 keq ha^{-1} yr^{-1}.

Despite the widespread increases in ANC, Figure 5.16 illustrates that levels have yet to reach the widely applied critical limit at several AWMN sites. In their assessment of recovery using two different physico-chemical models (SSWC and FAB), Kernan *et al.* (2010) estimate that the critical load at around one-third of AWMN sites will still be exceeded in 2020.

Table 5.7: Freshwater acidity critical load exceedances by site and country. Source CEH/RoTAP.

Country	Number of FAB sites	Number and percentage of sites exceeded by acid deposition			
		1986-88	1996-98	2006-08	2020
England	425	289 (68%)	267 (63%)	232 (55%)	209 (49%)
Wales	344	278 (81%)	229 (67%)	158 (46%)	117 (34%)
Scotland	856	403 (47%)	307 (36%)	200 (23%)	130 (15%)
Northern Ireland	127	28 (22%)	30 (24%)	21 (17%)	18 (14%)
UK	1752	998 (57%)	833 (48%)	611 (35%)	474 (27%)

A Generalised Likelihood Uncertainty Estimation (GLUE) approach has been used to estimate the uncertainties in the HARM acid deposition model (Page *et al.*, 2008) and assess the robustness of ecosystem protection offered by future emissions reductions (see Section 4.4, Uncertainty, in Chapter 4). Emissions for 2005 and 2020 were taken from the NAEI and EMEP for UK and Europe, respectively. Under these assumptions, UK emissions of SO_2 and NO_x declined by 54% and 44% respectively over this time interval, with NH_3 emissions being held constant.

Despite the large uncertainties in modelled deposition estimates, the reduction in acidic emissions between 2005 and 2020 has produced a statistically significant reduction in critical loads exceedances for the 1752 surface water bodies in the FAB dataset. Since the adopted methodology incorporates CBED deposition estimates, the uncertainty estimations presented here are likely to be comparable for the similarly structured FRAME model. For similar levels of emission reductions, FRAME estimates of reductions in future critical loads exceedances for freshwaters are likely to be statistically significant.

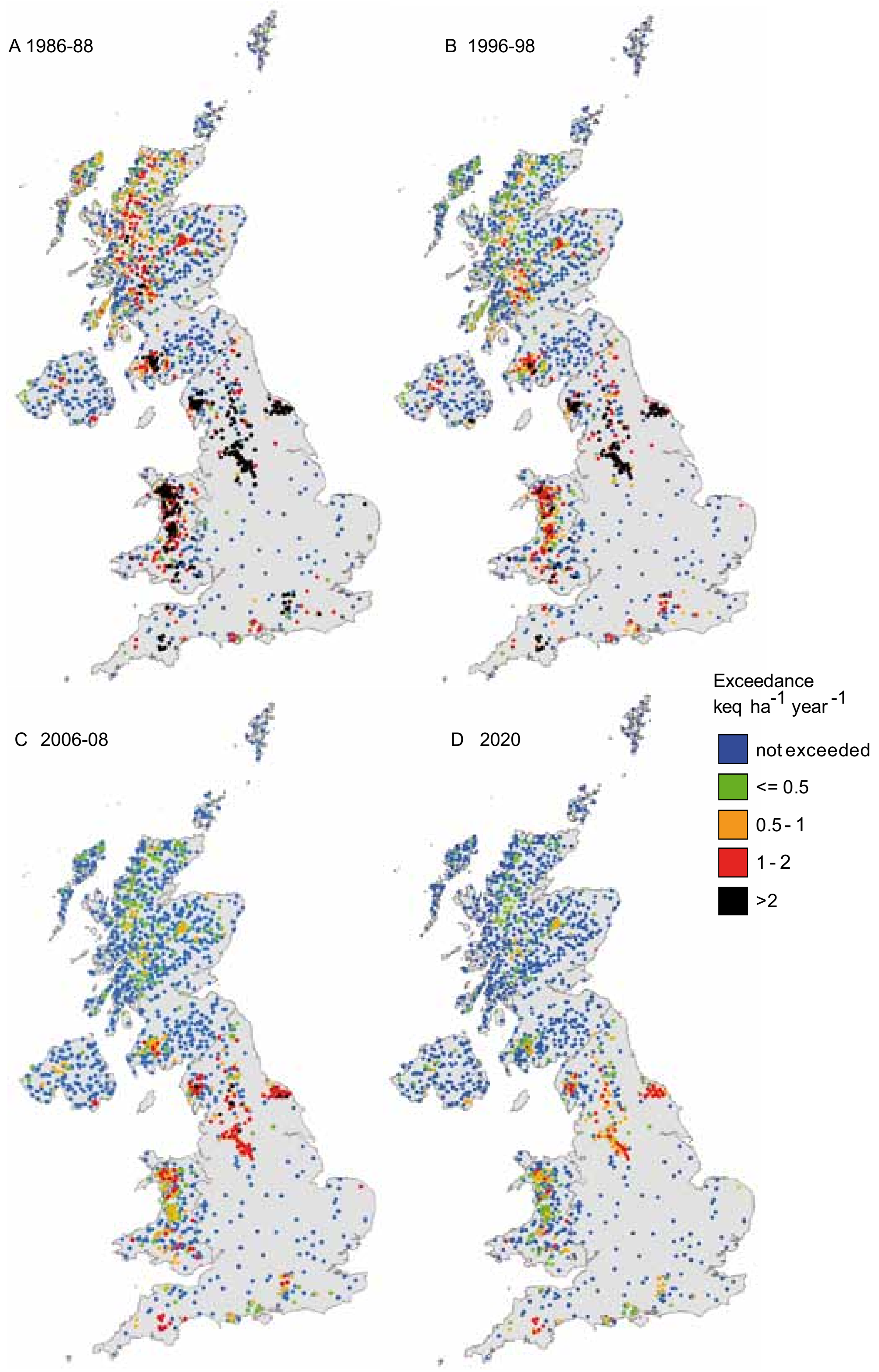

Figure 5.23: Exceedance of acidity critical loads for freshwaters by acid deposition for (a) 1986-88, (b)1996-98, (c) 2006-08 and (d) 2020. Source CEH/RoTAP.

5.3.8 Nitrogen deposition and eutrophication of upland water ecosystems

Several studies in recent years have challenged the view that phosphorus (P) inputs alone stimulate the eutrophication of lakes (e.g. Schindler, (1977). In some alpine and Arctic lakes in North America, N deposition has been proposed as a major cause of changes in phytoplankton communities (e.g. (Baron *et al.*, 2000; Fenn *et al.*, 2003; Saros *et al.*, 2005; Sickman *et al.*, 2003; Wolfe *et al.*, 2001) with evidence based on diatom and isotopic analysis of lake sediment ^{15}N. Similar studies in the UK reached the same conclusions (Curtis and Simpson, 2007).

Lake nutrient chemistry and chlorophyll-*a* data from Scandinavia and North America have revealed higher phytoplankton biomass relative to total P concentration where N deposition levels are elevated (Bergström *et al.*, 2005; Bergström and Jansson, 2006). In the UK, phytoplankton growth rate and yield limitation by N and P in 30 upland lakes was tested directly in laboratory incubations and with *in situ* nutrient diffusing substrata for periphyton by Maberly *et al.* (2002), and the study was subsequently supplemented by data for an additional 13 lakes (Curtis and Simpson, 2007). Across the 43 sites, growth and productivity were limited almost as frequently by N availability as by P but joint- or co-limitation of growth by both N and P together was the most common status. These bioassay studies support the assertions of Bergström and Jansson (2006) that N limitation is widespread in upland lakes and that even P-limited sites may once have been N-limited but are now so modified by anthropogenic N deposition their nutrient status has changed. The AWMN site Scoat Tarn is an example of a lake currently showing P limitation of phytoplankton growth which may have been induced by high levels of nitrate leaching resulting from large deposition loads of total N (Curtis and Simpson, 2007), i.e. the lake may have historically been N-limited.

These studies demonstrate the potential role of atmospheric N deposition in changing algal productivity and nutrient regimes in upland lakes, with implications for N emissions policy with respect to several international directives. For example, nutrient-poor lakes in the UK uplands designated under the EU Habitats Directive may be undergoing changes that may also be considered a deviation from the good ecological status required under the EU Water Framework Directive.

5.4 Effects on vegetation

5.4.1 Introduction

A range of aerial pollutants can affect vegetation, especially around individual sources, but the focus of this chapter is on the pollutants for which thresholds for effects are exceeded across large areas of the UK countryside – nitrogen deposition and ozone. Contaminants such as hydrogen chloride or hydrogen fluoride are only of concern close to sources, while there is also little evidence of adverse effects at current levels of metal deposition on vegetation in the UK. Historically, concentrations of sulphur dioxide (SO_2) were sufficient to have adverse effects on sensitive species, especially lichens and bryophytes, in many areas of the UK, but concentrations have fallen dramatically over the last 25 years (see Chapter 3). The implications of this for vegetation are considered in Chapter 8. The effects of gaseous components of nitrogen deposition and of ozone are considered in more detail in this chapter.

5.4.2 Nitrogen deposition

As described in Chapter 3, N deposition can occur in the oxidised or reduced form; both forms can be dry deposited as gases and particles or wet deposited in rain, mist or snow. In evaluating effects on vegetation, it is important to consider whether effects are due to the total deposition input of N or to particular components. Direct toxic effects of nitric acid (HNO_3) are unlikely under UK conditions (Bytnerowicz *et al.*, 1998) given that most deposition of HNO_3 is to external leaf surfaces and concentrations are small. Gaseous concentrations of nitrogen oxides (NO_x, i.e. NO and NO_2) may exceed critical levels in the UK but this is limited to areas within cities or close to major roads. By contrast, concentrations of ammonia (NH_3) exceed revised critical levels over large areas of the UK, and these effects are considered in more detail later in this section.

The mechanisms by which N deposition affects vegetation have important implications for the interpretation of experimental and field data. At high levels of deposition, NH_3 may have direct toxic effects on plants (Krupa, 2003); however, even at lower levels, effects on vegetation can be widespread. Since nitrogen is the limiting nutrient for plant growth in many terrestrial ecosystems, an excess of reactive N deposition to these ecosystems may increase growth and carbon sequestration. However, this can also change species composition, and may reduce species richness, by favouring species adapted to quick exploitation of available nutrients (Tilman *et al.,* 1982), by increasing the biomass of all species and thus 'thinning out' smaller individuals (Stevens and Carson, 1999), or by a combination of these mechanisms. Nitrogen deposition may also lead to plant nutrient imbalance (e.g. inducing P limitation (Phoenix *et al.,* 2003)), soil acidification (Bobbink *et al.*, 2010), changes in the rates of soil microbial processes (Aber *et al.*, 2003) or increased susceptibility to environmental stressors such as diseases, pests or late winter injury (e.g. Carroll *et al.* (1998); Power *et al.* (1999)). The importance of these different mechanisms varies with the species or community of concern and the physical and chemical form of the deposition.

Over the last 15 years, a substantial amount of new research on the impacts of N deposition has been conducted in the UK[10]. This research broadly falls into two types of investigation – long-term field manipulation experiments, in which nitrogen deposition is artificially increased, mostly in the form of wet deposition, and field surveys which use spatial gradients or temporal changes in both wet and dry N deposition. In experimental studies, single factors are experimentally altered and the ecosystem response measured. If we observe a change in a response variable, we can infer with some confidence that the manipulated variable is a driver that has caused the change, and we can say how long it takes for the system to respond to that driver. However, experimental studies are biased toward relatively short-term responses (even the longest experiments seldom exceed 20 years), and substantial atmospheric N deposition has been occurring in the

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[10] see http://www.bangor.ceh.ac.uk/terrestrial-umbrella/ for studies supported by Defra under the UKREATE programme

UK since 1850 (Fowler *et al.*, 2004). Artefacts of the manipulation itself (such as high concentrations of the applied pollutant) or site-specific factors might explain part of the response. A complementary approach is through surveys of sites, either spatially along a gradient of N deposition, or by revisiting sites over time. Such field surveys can potentially provide information on longer-term responses, but they cannot tell us precisely when those responses occurred after the onset of the stress, nor can they determine causality; for these insights controlled experiments are required. In addition, gradients of N deposition may be highly correlated with those of other potential drivers (e.g. climate or management intensity) which need to be measured or controlled for, either through survey design or statistical analyses. National records have shown changes in the distribution of both vascular and lower plants over recent decades (Braithwaite *et al.*, 2006), but these data have not been subject to statistical analysis to test the hypothesis that nitrogen deposition is a significant driver of the observed changes. Hence we have not considered them in our detailed analysis, but do consider the implications of their findings in broader interpretation of the more targeted surveys.

Here we provide an overview of key findings from long-term experiments and targeted field surveys on the effects of nitrogen deposition in the UK, and evaluate their implications in terms of key policy questions, including the relative importance of different components of deposition. This section does not provide a detailed review of all the evidence of effects of N deposition; Bobbink *et al.* (2010) provide an authoritative overview of the impacts of N deposition on ecosystems worldwide, based on a sythesis of recent evidence.

Field manipulation experiments

The UK has had nine long-term field manipulation experiments that simulate increased rates of atmospheric N deposition through regular applications of N solution (and in one case release of gaseous NH_3) to experimental plots over a number of years. These experiments cover heathland, bog and grassland ecosystems and represent some of the UK's most important and widely distributed semi-natural habitats. An overview of the findings to date indicates a number of consistent responses between the contrasting ecosystems. Soil responses have also been studied in these experiments (see Section 5.2.2), and some of the experiments have also investigated responses to decreases in N loading (see Section 8).

The highest sensitivity to nitrogen addition has generally been observed in lower plants (Table 5.8), which is most apparent as a decline in lichen cover in heathland and bog sites and a decline in bryophyte cover in the grasslands (Arroniz-Crespo *et al.*, 2008; Britton and Fisher, 2007; Carroll *et al.*, 2000; Emmett *et al.*, 2007; Pilkington *et al.*, 2007; Power *et al.*, 2006). Hypnaceous mosses show some increases at Whim bog, which may reflect their tolerance to elevated N deposition (UKREATE, 2010; Wilson, 2003), while at Budworth lowland heath there is also evidence of increases in bryophyte cover, although this may not be a linear response, with bryophytes declining at the highest N doses (Wilson, 2003). At Newborough dune grassland, the biomass of bryophytes (a parameter not included in Table 5.8) increased (Plassmann *et al.*, 2009). Lower plants also show the clearest increases in tissue N concentrations: this is observed at all sites where measured.

Among the five sites dominated by the ericacous shrub *Calluna vulgaris*, there has generally been little change in higher plant community composition in response to increased wet N deposition, although N deposition has increased growth and/or cover of *Calluna vulgaris* at these sites, often in conjunction with earlier or faster spring growth (Britton and Fisher, 2008; Britton *et al.*, 2008; Carroll *et al.*, 1999; Pilkington, 2003; Power *et al.*, 2006; Sheppard *et al.*, 2008; Wilson, 2003). The main contrast is the loss of *Calluna* observed when N is applied as dry-deposited NH_3 at Whim, which allows an increase in the graminoid *Eriophorum vaginatum* (Sheppard *et al.*, 2009). At the grassland sites, Table 5.8 shows that there is some tendency for community change to follow the pattern of increased graminoid dominance at the expense of forbs. In Pwllpeiran acidic grassland, this is seen as a reduction in the cover of the ericaceous shrub *Vaccinium myrtillus* concurrent with an increase in sedge abundance (although the grass *Nardus stricta* declines) (Emmett *et al.*, 2007). In the acidic and calcareous grasslands at Wardlow, plant community responses to N deposition have been relatively slow, but a general increase in grass cover with declines in forbs has begun to emerge (Carroll *et al.*, 2003; Morecroft *et al.*, 1994; O'Sullivan, 2008). P or co-NP limitation possibly explains the slow responses at the Wardlow grasslands and absence of graminoid increases at Newborough. Despite these changes, in no experiment across all grassland, heathland and bog sites, has any higher plant species been completely lost from N-treated plots, the only exception being when the experiment involved gaseous NH_3 rather than wet deposition, as discussed in more detail in a later section. However, a reduced cover or abundance of species in relatively small N-manipulation plots may have implications for their continuing presence in the context of a wider N-impacted landscape.

Evidence of increased tissue N concentrations in higher plants has been found at most sites, although such increases are not necessarily true for all species or all years sampled. At Ruabon upland heath and Budworth lowland heath, *C. vulgaris* tissue N tends to increase in an N-dose-dependent manner, but significant differences are not always apparent at the lower N doses (Pilkington *et al.*, 2005; Wilson, 2003), while at Culardoch low alpine heath, *C. vulgaris* tissue N consistently increases with N dose (Britton *et al.*, 2008). At Thursley lowland heath and Whim bog, *C. vulgaris* shoot N concentrations again increase with N dose, but not consistently each year at Whim (Power *et al.*, 1995; Sheppard *et al.*, 2008). At the acidic and calcareous grasslands of Wardlow, increases in tissue N concentrations have been observed (Carroll *et al.*, 2003; Morecroft *et al.*, 1994), but such changes are not apparent in many species even in the long term (O'Sullivan, 2008). There has been little evidence of increases in tissue N at Pwllpeiran acidic grassland or Newborough dune grassland (Emmett *et al.*, 2007; Plassmann *et al.*, 2009).

Increases in tissue N in *C. vulgaris* may partially drive secondary stresses and damage in *C. vulgaris* at heathland and bog sites, seen as greater frost and/or winter desiccation damage, increased damage from heather beetle or increased incidence of pathogen damage (Britton and Fisher, 2007; Carroll *et al.*, 1999; Sheppard *et al.*, 2008).

Flowering also shows some consistency in response to enhanced N deposition, but responses vary depending on the functional group. At heathland sites, N deposition has increased flowering of *C. vulgaris* (Britton and Fisher, 2008; Cawley, 2000; Power *et al.*, 1995), whereas at both the acidic and calcareous grasslands at Wardlow, large reductions in forb flowering have occurred, which are greater than effects on vegetative growth (O'Sullivan, 2008).

5.4.3 Field surveys

Two different designs of field survey can be distinguished. Regional spatial surveys measure sites at a similar time over a spatial gradient of the driving variable. Such surveys use a 'space for time substitution' in which it is assumed that differences observed over a spatial gradient of the driver from low to high levels can be proxies for changes at a single site over time. A second approach is to resurvey sites for which historical records of vegetation composition exist, or to establish permanent quadrats that are monitored at regular intervals. This approach in principle allows the effects of changing rates of nitrogen deposition to be assessed, although other drivers that may change over the time period (e.g. management) need to be considered.

In order to provide a common basis for comparisons between a range of surveys in different ecosystems we consider here the relationship between nitrogen deposition and the species richness and cover of major functional groups of plants. Clark and Tilman (2008) and Bobbink *et al.* (2010) provide further discussion of this approach. Species richness is the mean number of species in a standard number of sampling units at each site (e.g. five 2 m^2 or 1 m^2 quadrats); cover is the average percentage area of each sampling unit occupied by a species or a group of species. It is important to note that species richness refers to the *mean number* of species in a particular sampling unit, but not the species *identity*. Thus a decline in species richness does not necessarily indicate a local extinction of any particular species, but it does mean that fewer individuals of at least some species occur in the landscape. Some surveys have used additional statistical tests to determine which, if any, species are consistently more or less frequent in areas receiving higher levels of N deposition. As in Section 5.4.2, we group changes in cover into function groups of forbs, bryophytes, lichens, ericoids and graminoids.

Regional surveys

Eight regional surveys focused on particular plant communities in the UK are considered, as well as three broad vegetation types covered in the most recent years (1998, 2007) of the Countryside Survey (Table 5.9). Except where noted in Table 5.9, deposition rates are provided by the CBED 5 km × 5 km scale dataset, a measurement-based model of pollutant deposition in the UK (see Chapter 4). The surveys also consider to a varying extent other potential drivers of species richness and cover, including climate (e.g. annual rainfall or temperature), deposition of other pollutants, site attributes (e.g. altitude, soil pH) and management (e.g. grazing intensity). Different surveys also cover different ranges of N deposition, and those that cover a narrower range of N deposition have less power to detect significant relationships. Finally, since the focus of the Countryside Survey (CS) is on documenting changes in a representative sample of the British countryside, rather than in specific plant communities, CS sites overlap a broader variety of habitats, land uses and other drivers of diversity than the other surveys.

Of the eleven regional surveys considered, seven show a significant decline in overall species richness with increasing N deposition (Table 5.9). Habitats showing a decline include grassland (acid grassland: AGS; mixed grassland: CS-Grass), heather moorland

Table 5.8: Summary of key ecosystem responses in nine N deposition simulation experiments in the UK (The responses presented here are for selected components that have been measured at most sites, enabling inter-site comparisons and revealing overall trends. Arrows ↑ˉ indicate direction of response detected; o indicates no response; blank boxes indicate response not measured. Responses in parentheses indicate change is restricted to a few instances (see text for details). The dose at which response is observed varies between sites).

	Ruabon upland heath	Budworth lowland heath	Thursley lowland heath	C'lardoch low alpine heath	Whim bog Wet* Dry*	Wardlow calc. grassland	Wardlow acidic grassland	Pwllp'an acidic grassland	Newboro' fixed dune
Bryophyte cover	↓	(↑↓)	o		(↑)↓(↓)↓	↓	↓	(ˉ)	o
Lichen cover	↓	o	↓	↓	↓ ↓				
Calluna cover &/or growth	↑	↑	↑	↑	↓ ↓				
Graminoid cover	o	o	o	o	(↓) (↑)	↑	↑	↑↓	
Forb cover						↓	↓	(↓)	o
Lower plant foliar N	↑	↑	↑		↑ ↑		↑		↑
Higher plant foliar N	↑	↑	↑	↑	↑ ↑	↑	↑	o	o
Flowering	↑	↑	↑	↑		↓	↓		
Calluna injury/stress	↑		↑	↑	o ↑				

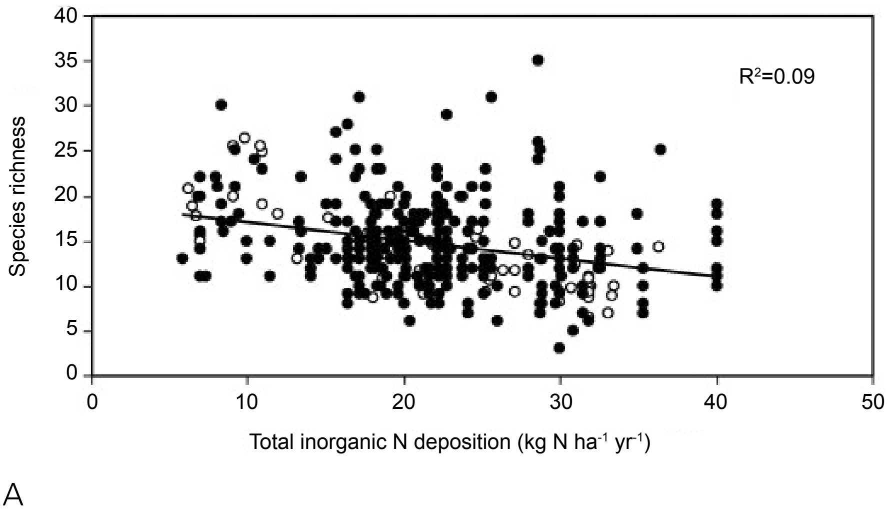
Table 5.9: Summary of significant relationships between N deposition and plant species richness and cover in regional or national surveys (Arrows ↑¯ indicate direction of response detected; o indicates no response; shaded boxes indicate response not measured or not reported. The lowest level considered as significant is $p<0.05$ (i.e. some relationships shown in table are significant at $p<0.01$ or $p<0.001$). Refer to notes below table for further information on all surveys).

	AGS	CGS	CMS	RHS	SDS	WES	SMont	SMoor	CS-Grass	CS-H/B	CS-Wood
N-deposition[1]	5-35[2]	5-39	6-31	7-40	7-29	10-53	8-22	5-20	4-42	4-42	9-57
Species richness	↓	o	↓	o	↓	o	o	↓	↓	↓	↓
Forb cover	↓			↑	↑		o	o	o	↑	↑
Forb richness	↓	o	↓	↑			↓	↓			
Bryophyte cover	o			-		o	↑	o	o	↑	o
Bryophyte richness	o	o	↓	o		o	↑	o			
Lichen cover				o		o	o	↓			
Lichen richness		o		o		o	o	↓			
Ericoid cover				↑			↓	o		↑	
Ericoid richness			o	↑			↓	↓			
Graminoid cover	o			↑	↑		↑	o	↑	↑	↓
Graminoid richness	-	o	o	↓			o	↓			

KEY: AGS = Acid Grassland Survey: 68 acid grasslands (NVC type U4) sampled across Great Britain over 2002 and 2003 (Stevens *et al.*, 2006; Stevens *et al.*, 2004). **CGS** = Calcareous Grassland Survey: calcareous grasslands (mainly NVC CG1 and 2) sampled across Great Britain in 2006/07 (UKREATE, 2010; van den Berg *et al.*, in press). **CMS** = *Calluna* Moorland Survey: 36 *Calluna* heather moorlands sampled across northern Great Britain over 2005-06 (Edmondson, 2007; Edmondson *et al.*, 2010). **RHS** = *Racomitrium* Heath Survey: 22 *Racomitrium* heathlands sampled across northern Great Britain in 2007-08 (Armitage, 2010) **SDS** = Sand Dune Survey: 11 coastal dune grasslands sampled in England and Wales in 2002 (Jones *et al.*, 2004). **WES** = Woodland Epiphyte Survey: 7 Atlantic oak woodlands sampled in Scotland and the north of England for epiphytic moss, liverwort and lichen communities, measured in 2002 (Mitchell *et al.*, 2005). **SMont** = Scottish Montane Survey: sites sampled across Scotland in 2006 (UKREATE, 2010). **SMoor** = Scottish Moorland Survey: sites sampled across Scotland in 2006 (UKREATE, 2010). **CS-Grass** = Countryside Survey mixed grasslands: about 2000 plots sampled across Great Britain in 1998 and 2007 (Carey *et al.*, 2008). **CS-H/B** = Countryside Survey heath and bog: about 2000 plots sampled across Great Britain in 1998 and 2007 (Carey *et al.*, 2008). **CS-Wood** = Countryside Survey broadleaved woodland: about 800 plots sampled across Great Britain in 1998 and 2007 (Carey *et al.*, 2008).

ADDITIONAL NOTES: 1. N deposition in kg N ha^{1} yr^{1}. 2. For **AGS**, N deposition is the most significant correlate to species richness and cover of 20 potential drivers on diversity tested. Graminoids show a trend toward increasing cover with increasing N input, although non-significant. Although overall bryophyte cover and richness do not change, the cover of different species changes. 3. For **CGS**, graminoid/forb ratio increases with N deposition, although effects on graminoid and forb species richness are not significant. 4. For **CMS**, study was focused on bryophytes: species numbers of ericoids and graminoids were low, and may be impacted in some areas by management, thus masking potential impacts of N deposition. 5. For **RHS**, strongest response to N deposition is bryophyte cover decline; responses in other groups were much smaller ($r^2<10\%$). Results in Armitage (2010) include Europe-wide relationships showing additional significant declines in forb richness, bryophyte richness and lichen cover, and no change in forb cover, with increasing N deposition. 7. For **SMS**, only the forb *Hypochaeris radicata* was reported. 6. For **WES**, there are too few sites to detect significant relationships, although there is a trend of decreasing bryophyte cover with increasing N deposition, from 66.0% at an N deposition rate of <20 kg N ha^{-1} yr^{1} to 40.0% at a rate of >20 kg ha^{-1} yr^{1}. This trend is especially prominent for liverworts, which average 30.5% cover and 6.3% cover, respectively, over these two ranges of N deposition.

(*Calluna* moorland: CMS; Scottish moorland: SMoor; mixed heath and bog: CS-H/B), sand dunes (SDS), and broadleaved woodland (CS-Wood). Figure 5.24 shows relationships between N deposition and species richness for three of the surveys, in acid- and mixed-grassland (AGS and CS-Grass, Figure 5.24a), and bryophytes in heather moorland (CMS, Figure 5.24b). In Figure 5.24a, data from the Acid Grassland Survey, which is focused on a specific grassland community, is shown embedded in data from the much more comprehensive Countryside Survey. This shows a clear consistency in the relationship derived from the two datasets, despite the much greater scatter in the CS dataset.



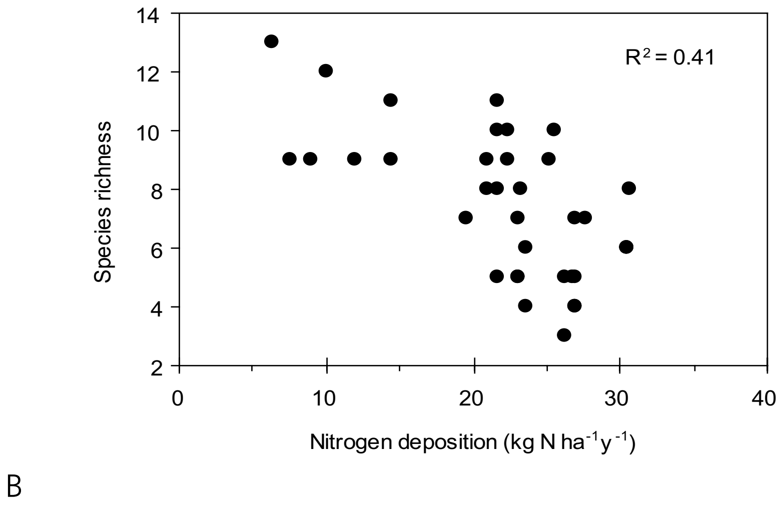


Figure 5.24: (a) Species richness per 2 x 2 m quadrat against N deposition (kg N ha^{-1} yr^{-1}) for Countryside Survey (●) ($r^2=0.04$) (Stevens *et al.*, 2009) and survey of Stevens et al. (2004) (○) ($r^2=0.55$). (b) Relationship between bryophyte species richness and N deposition at 36 Calluna moorland sites in northern Britain 2005-06 (Edmondson, 2007).

Even with the statistical tools used to account for other variables, it is possible that relationships observed in the surveys are driven by factors other than N deposition. Although it is not possible to determine causality by surveys alone, closer examination of some surveys can provide insight into the processes involved. In the CS mixed grasslands, the strongest relationships are found for acid grasslands, with a weak (but significant) negative association found for mesotrophic grassland, and no significant relationship for calcareous grasslands when other explanatory variables are considered (Maskell *et al.*, 2010). Nitrogen deposition can have both acidifying and eutrophying effects, and one possible interpretation is that the main impact of N deposition on grasslands is through accelerated soil acidification (to which calcareous grasslands are often well-buffered) rather than eutrophication. More detailed analysis of the responses of individual species in the Acid Grassland Survey (AGS) provides some support for an important role of acidification in acid grasslands (Stevens *et al.*, 2010).

Three surveys showed no relationship between species richness and N deposition. In the Scottish Montane (SMont) and *Racomitrium* Heath (RHS) surveys, increases in the species richness in some functional groups are counterbalanced by declines in other groups, leading to no overall change. In the RHS, a strong decline in the cover of *Racomitrium* moss occurs in areas with higher rates of N deposition. Since *Racomitrium* normally forms a thick mat in these heathlands, its decline is thought to expose more soil for vascular plants. There are no significant changes in overall species richness in the Woodland Epiphyte Survey (WES), but species composition does change, and bryophytes, particularly liverworts, show a non-significant decline in cover at N deposition levels above 20 kg N ha^{-1} yr^{1} (Mitchell *et al.*, 2005).

The relationship between species richness and N deposition appears to be dominated by changes in the species richness of forbs, which decline in four out of the six ecosystems considered. (The exceptions to this are the RHS and Calcareous Grassland Survey (CGS), for reasons described above.) For example, in the AGS the forbs *Plantago lanceolata* (ribwort plantain), *Campanula rotundifolia* (harebell) and *Euphrasia officinalis* (eyebright) are found at lower frequency in the high-N deposition sites. However, with the exception of the AGS, forb cover shows either an increase or no change with N deposition. This may reflect increases in the cover of more pollution-tolerant species compensating for the decrease in species number. Ericoid cover and richness show both increases and decreases with increasing N deposition, perhaps because site management may play a stronger role for ericoids than atmospheric deposition.

Another general feature of the regional surveys is an increase in the cover of graminoids (noted in five out of eight surveys). Combined with the decline in overall species richness, this is consistent with a decline in the frequency of acid- or N-sensitive species compensated by an increase in the cover of grass or sedge species that are more tolerant to these conditions. For the early-successional stage dune grasslands (Sand Dune Survey, SDS), the observations can also be interpreted as accelerated succession due to nitrogen input, and are consistent with observed increases in carbon and nitrogen status in soils.

With increasing nitrogen deposition the species richness of bryophytes declines strongly in the *Calluna* Moorland Survey (CMS) (Table 5.9, Figure 5.24b), shows an increase (together with cover) in the Scottish Montane Survey (SMont) and no change elsewhere. It is possible that the discrepancy between the CMS and SMont results is due to different ranges, as well as cumulative doses, of N deposition: the strongest decline in species richness in the CMS occurs at the highest levels of N deposition (see Figure 5.24). There is a strong decline in the cover of *Racomitrium* moss in the RHS, but elsewhere either increasing trends or no change in bryophyte cover. In the AGS, the pollution-tolerant moss *Hypnum cupressiforme* increases in frequency and cover at higher levels of N deposition.

With the exception of the Scottish Moorland Survey, lichen richness and cover show no relationship to N deposition. It is apparent from several studies that a significant shift in species composition from pollution-sensitive species toward more pollution-tolerant bryophyte and/or lichen species occurs with increasing N deposition, although total species number may not be affected. This suggests that the community composition of lower plants can shift more dynamically in response to pollution than that of vascular plants.

Resurveys

Table 5.10 summarises the results of national- and regional-scale studies in which changes in vegetation composition over different time periods have been related statistically to a range of potential drivers, including modelled nitrogen deposition. If we assume that the relationships between N deposition and species richness in recent spatial surveys are at least partly causal, comparison with past spatial surveys can provide insight into whether or not the changes observed are recent. The results of the studies summarised in Table 5.10 should be related to those in the equivalent spatial surveys as summarised in Table 5.9.

In contrast to the results from the regional spatial surveys shown in Table 5.9, for the four targeted surveys listed in Table 5.10 there are few significant relationships with overall species richness or forb species richness. This suggests that much of the decline in overall species richness, and that of different functional groups, shown in Table 5.9 had already occurred by the 1970s. The exception is the Scottish Moorland Survey, in which overall species richness decreased between the 1960s/1970s and 2004/06 in sites with higher rates of N deposition, with declines also in the species richness of grasses and lichens. For the Scottish Montane Survey, the only recent change is a decline in lichen species richness in some habitats; all other trends shown in Table 5.9 existed over 30 years ago. As shown in Table 5.10, both these Scottish surveys were conducted in an area of the country with relatively low N deposition, which might explain the more recent responses to cumulative N deposition.

The only study to systematically assess changes in species composition at regular intervals rather than between two periods is the Countryside Survey (CS). Table 5.10 summarises data for the 20-year period 1978-98 and for the most recent decade 1998-2007. The CS analysis suggests that the decrease in overall species richness of broadleaved woodlands and heath and bog habitats was already evident in the 1970s. In grasslands, a significant decrease in species richness with increasing N deposition was already evident in the 1978 survey, but the recent responses are more complex, with a decline in species richness between 1978 and 1998, and an increase in the most recent period. Between 1978 and 1998, the further decline in species richness in grasslands was associated with an increase in Ellenberg nutrient index, confirming a small but significant additional impact of N deposition. In broadleaved woodland, there was also evidence of a further decline in bryophyte and grass species richness between 1978 and 1998, although overall species richness did not decline.

The lack of major changes in species richness and (when measured) cover of the major functional groups over the last 30 years shown in most of the resurveys may also be associated with the evidence of declines in soil acidity that are reported in soil surveys: soil pH increases would, on the whole, be expected to slow or mitigate the rate of species richness reduction due to N deposition (Stevens *et al.*, 2004). Van den Berg *et al.* (in press) also found that soil pH had similarly reduced the effects of N deposition on changes in diversity and evenness in calcareous grasslands. In terms of vegetation composition, the evidence of limited change over the last 10-20 years from the UK Environmental Change Network (ECN) (Morecroft *et al.*, 2009) is consistent with the evidence in Table 5.10, and increases in soil pH have occurred at several of these sites. In the more extensive CS dataset, there is evidence that the mean Ellenberg R (acidity) index of the vegetation has increased over the period 1978-2007 on plots which have shown an increase in pH, suggesting that a recovery in soil pH is also directly associated with changes in vegetation composition.

In these repeated surveys which assessed the responses of individual species, there was a consistent pattern for species adapted to low nutrient habitats to continue to decline in cover in areas of high N deposition, and for species adapted to higher nutrient environments to increase in cover (Table 5.10). In the CGS, there was also an effect of N deposition on change in plot evenness and the Shannon diversity index, despite the lack of effect of species richness, suggesting an effect on the vegetation composition. The effects on individual species agree with evidence from from the Atlas of the British Flora, which compiles national records of species presence in 10 km grid squares. This shows that species with a low Ellenberg N (fertility) index tended showed a decrease in their distribution between 1930/69 and 1987/99 compared to average species (Preston *et al.*, 2002), although the analysis has not partitioned the effects of atmospheric N deposition from other drivers of fertility change such as more intensive management. Dupre *et al.* (2010) also provide evidence that changes in species richness and composition in acid grasslands in north-west Europe over the past 70 years are associated with increased N deposition.

The results from targeted national-scale surveys over time suggest that current rates of N deposition are associated with further declines in the cover of sensitive species even when there is no decline in species richness. These results, taken together with the relationships between N deposition and differences in cover of different functional groups that were identified in the spatial surveys and the changes in Ellenberg R and N values over time, suggest that the plant species composition of terrestrial habitats is changing in the UK in response to continued N deposition, and possibly to decreasing acid deposition.

Table 5.10: Summary of effects on species richness and cover in regional or national studies which have resurveyed the same plots at different periods of time differing by more than 10 years (Results from the spatial analysis of these surveys, with further details and references, are in Table 5.9.)

Parameter	WRS	CGS	SMont	SMoor	CS1	CS2
Time period	1971-2001	1992/93-2006/09	1970s-2004/06	1960s/1970s-2004/06	1978-98	1998-2007
Species richness	ns	ns	ns	Negative	ns (hb, bw) negative (g)	ns (hb, bw) positive (g)
Grass cover/richness	ND	ns	ND	negative (richness) ns (cover)	ns (hb, g) negative (bw)	ns (hb, bw) positive (g)
Forb cover/richness	ND	ns	ND	ns (richness)	ns (hb, g, bw)	ns (hb, bw) positive (g)
Ericoid cover/richness	ND	ND	ns	ns (richness and cover)	ns (hb)	positive (hb)
Bryophyte cover/richness	ND	ns (frequency)	ns (richness)	ns (richness)	ns (hb) negative (g, bw)	ND
Lichen cover/richness	ND	ns	negative (richness)	positive (richness)	ND	ND
Ellenberg N	ns	ns	ND	ND	positive (hb, g)	ns (hb, g, bw)
Changes in cover or frequency of individual species	Positive for 6 high N and negative for 6 low N species	negative for 5 low N species	ND	ND	26 negative, 12 positive overall; for low N species, 20 negative and 3 positive	ND

NOTES: ns – not significant, ND – not determined; **WRS**: Woodland Resurvey (Kirby *et al.*, 2005): 103 plots of native woodland in Great Britain. **CGS**: see Table 5.9. **SMont** and **SMoor**: see Table 5.9. **CS1** and **CS2**: Countryside Survey results for heathlands and bogs (hb), grasslands (g) and broadleaved woodlands (bw); for details see Table 5.9. The effects on lichen richness in **Smont** were only found in *Nardus* grassland and *Vaccinium* heath.

5.4.4 Does nitrogen deposition lead to a loss of diversity and of characteristic plant species?

Taken together, the results from both spatial surveys and temporal resurveys suggest that:

i. the species richness of many grasslands, heathlands and woodlands was already in decline at least 30 years ago;
ii. the declining species richness of montane and moorland ecosystems in more remote areas of the country may be a more recent phenomenon;
iii. the overall species richness of forbs and graminoids is tending to decrease, whilst graminoid cover is tending to increase; and
iv. bryophyte and lichen species richness and community composition is more dynamic than that of vascular plants, with a replacement of more sensitive species by a more pollution-tolerant community.

The limitations of surveys in defining causal relationships mean that these conclusions should be considered as the basis for useful hypotheses that can be tested and supported with other lines of evidence, in particular from experimental studies. Field manipulation studies provide evidence of an increase in graminoid dominance at the expense of forbs in grassland systems (Table 5.8), but, in general, the observed changes in higher plant species are less consistent in experimental studies and in resurveys than in the spatial surveys. This may be because historical N deposition had reduced higher plant species richness before the experiments started in the 1980s and 1990s, especially in areas of relatively high N deposition.

Both field surveys and experimental studies show that hypnaceous moss species increase with increased N deposition. There is, however, a difference in the effects on lower plants between the different approaches; while the experimental studies consistently show effects on overall cover of bryophytes and lichens this is uncommon in the field surveys, in which it is more common for there to be changes in the species composition, with species adapted to low nutrient environments being reduced in cover or number compared to these adapted to higher nutrient environments. It is possible that the adverse effects in some field experiments using rates of deposition well above ambient are due to the toxicity of ammonium or nitrate which are present in high concentrations in the intermittent spray applications, as these groups of species may respond more to the aqueous concentrations of nitrogen species on their surfaces than to total deposition (Pearce and van der Wal, 2008). In addition, the effects of competitive exclusion of understorey species due to increased shading from faster-growing higher plants may be stronger in experiments than in the field, where nitrogen doses are lower and vegetation growth may be limited by factors such as grazing.

5.4.5 Critical load exceedance and effects on biodiversity

Figure 5.25 shows the percentage of the area of the UK for which the critical load for N deposition is exceeded in major sensitive habitats. The empirical critical loads used in this assessment were based on the ranges for different habitats proposed by Bobbink *et al.* (2003) which were based primarily on the risk of loss of characteristic species. The specific value selected within the range was based on expert judgement of UK habitats (Hall *et al.*, 2003). Results are shown from the mid-1980s to 2020. A substantial percentage (58%) of the total area of these conservationally important, low nutrient habitats is above the relevant critical load based on deposition data for 2006-08. These figures imply that N deposition is having significant adverse effects on these habitats across the UK countryside.

The critical loads that were used in this assessment were primarily based on experimental studies (Bobbink *et al.*, 2003). Bobbink (2008) has collated data from experimental studies and found for grasslands a linear relationships between species richness and exceedance of the relevant critical load; in boreal forest, there is no such relationship with species richness, although species composition does decline with increased exceedance, reflecting the loss of sensitive species. An important question therefore is whether the field evidence of the effects of N deposition in the UK is consistent with exceedance of the critical load leading to adverse ecological effects. The results from surveys summarised in Tables 5.9 and 5.10 provide clear evidence for several of the habitats shown in Figure 5.25 of the adverse effects of N deposition at rates of deposition which exceed the relevant critical load. However, interpretation of results of field surveys in terms of critical loads depends on the shape of the relationship between N deposition and species richness, or other relevant response measures. The critical load concept implies that there is a threshold deposition below which there will be no long-term effect, but the evidence from field surveys is that there is often little evidence of such a threshold or that a sigmoidal relationship might better fit the data (e.g. Figure 5.24a). Such non-linear responses, with greater reduction of plant species numbers at relatively low rates of deposition, have also been reported in some experimental studies (e.g. Clark and Tilman, (2008).

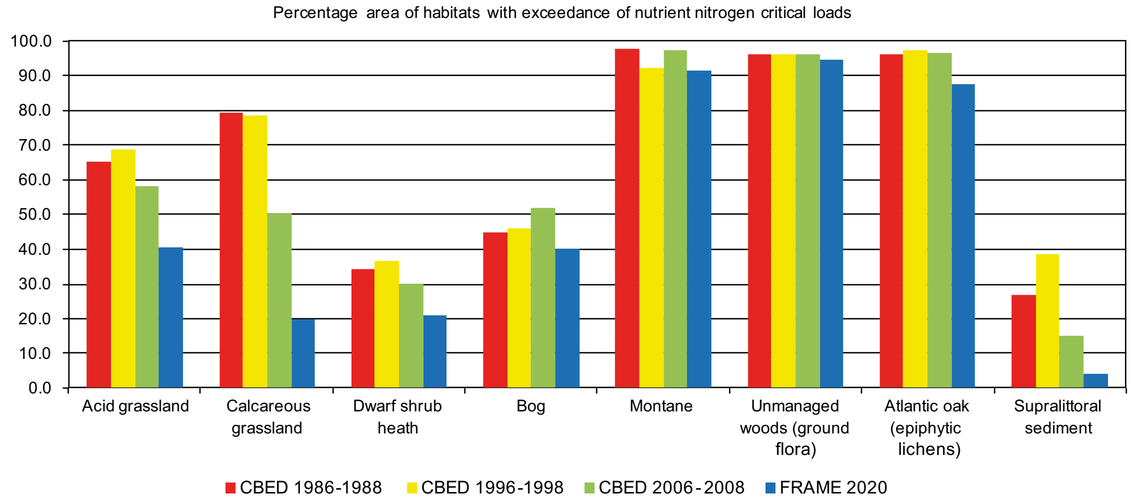


Figure 5.25: Exceedance of critical loads for effects of nitrogen deposition for sensitive semi-natural habitats. Source CEH / RoTAP. This figure shows the estimated percentage area of each major habitat with exceedance of the relevant critical loads in the mid-1980s, the mid-1990s, the mid-2000s and 2020. The critical loads used for this estimate were: 7 kg N ha^{-1} yr^{1} for montane (moss- and lichen-dominated summits); 10 kg N ha^{-1} yr^{1} for bogs and for epiphytic lichens (in Atlantic oak woods); 12 kg N ha^{-1} yr^{1} for woodland ground flora and dry dwarf shrub heath; 15 kg N ha^{-1} yr^{1} for wet dwarf shrub heath, acid grassland and supralittoral sediments (coastal dune grasslands); and 20 kg N ha^{-1} yr^{1} for calcareous grassland (Hall *et al.*, 2003).

It is projected that the percentage of the total UK area of sensitive habitats in which critical loads will be exceeded will decrease from 58% to 48% by 2020. However, the results shown in Figure 5.26 show substantial differences between habitats. For some habitats, such as bogs, montane habitats and woodlands, little decrease in critical load exceedance is predicted by 2020. In these habitats, adverse effects on N deposition on terrestrial biodiversity are likely to continue to 2020 and beyond, and further reductions in deposition will be needed before recovery can start. More intense management to increase rates of N removal could also play a role for actively managed habitats such as grasslands and heathlands, although there is evidence that management can have only a limited effect in mitigating the adverse effects of N deposition (e.g. (Plassmann *et al.*, 2009; Power *et al.*, 2006)). In contrast, for other habitats, such as calcareous grasslands, supralittoral sediments and dwarf shrub heath, the area in exceedance of the critical load is predicted to fall substantially by 2020. The nature and rate of change of species composition in response to reductions in critical load exceedance is uncertain (see Chapter 8 for further discussion) and monitoring of the responses to declining deposition in these habitats wll be very important.

However, while the synthesis of field surveys provides strong evidence of the adverse effects of N deposition on sensitive habitats across the UK, many of these studies were 'one-off' exercises, furthermore, the Countryside Survey was not specifically designed to evaluate the effects of air pollution on terrestrial biodiversity. There is no extensive monitoring network in the UK using standardised methods and covering a range of habitats that can provide consistent information on changes in the impacts of nitrogen deposition and other air pollutants in the UK. The value of such a network is clearly demonstrated by the long-term high quality data which has been provided for freshwater habitats by the UK AWMN. The establishment of a fully operational terrestrial network to assess the long-term effects of air pollution in the context of a changing climate, as recommended by NEGTAP (2001), remains a priority and needs to be based on indicators of both exposure and response. Over the past two years significant progress has been made by Natural England and the Countryside Council for Wales, in collaboration with the CEH staff responsible for the national management of the ECN, in developing a network of sites on National Nature Reserves for this purpose. Essentially a spatial extension of the current ECN (that carries out integrated physical, chemical and biological monitoring of 12 terrestrial sites), the Environment Change Biodiversity Network is intended to provide data according to ECN protocols for a reduced set of measurements, focusing specifically on the long-term effects of climate change and air pollution on vegetation and invertebrate indicator groups.

5.4.6 Do all forms of reactive N have the same effects?

The critical load for total N deposition makes no distinction between the forms in which N is deposited. Uptake of NH_3 into leaves might be expected to have different physiological effects to N uptake from soil but, until recently, there was no direct experimental comparison of different N forms. A unique experiment on an ombrotrophic bog at Whim in south-east Scotland (Leith *et al.*, 2004; Sheppard *et al.*, 2004) has now demonstrated that dry-deposited NH_3 has much greater effects (rapid accumulation of foliar N and loss of membrane integrity leading to a decline in cover) at the same rate of N deposition, than wet deposition of NH_4^+or nitrate-N on adjacent plots (Cape *et al.*, 2009; Sheppard *et al.*, 2009; Sheppard *et al.*, 2008). Figure 5.26 illustrates the much greater effects of gaseous NH_3, at a deposition rate of 24 kg ha^{-1} yr^{-1}, in terms of both positive and negative effects on the cover of major species, than both wet-deposited NO_3^- and NH_4^+. Although the experiment is confined to one ecosystem, an ombrotrophic bog, the three N-sensitive species (*Calluna*, *Sphagnum capillifolium* and *Cladonia portentosa),* which disappeared when NH_3-N deposition exceeded 24 kg N ha^{-1} yr^{1} (Sheppard *et al.*, 2009), are widespread and key components of many semi-natural ecosystems across the UK. These results suggest the possibility that gaseous NH_3 rather than wet-deposited N initiated the loss of *Calluna* from areas of the Netherlands and Denmark which had high concentrations of NH_3, although a more detailed comparison is needed of wet and dry deposition in these areas with those at Whim.

Furthermore, key findings from the Whim experiment are supported by field observations along transects from agricultural point sources of ammonia in the UK, in which effects on bryophytes, lichens and ground flora have been detected at relatively low NH_3 concentrations (Leith *et al.*, 2005; Pitcairn *et al.*, 2006; Pitcairn *et al.*, 1998). These recent results, combined with experimental and field data from other European countries, have led the UNECE to change the critical level for NH_3 gas (the threshold concentration for effects) from 8 μg m^{-3} as an annual average to 1 μg m^{-3} for bryophytes and lichens, and 3 μg m^{-3} (uncertainty range 2-4 μg m^{-3}) for understorey herbaceous plants (Cape *et al.*, 2009).

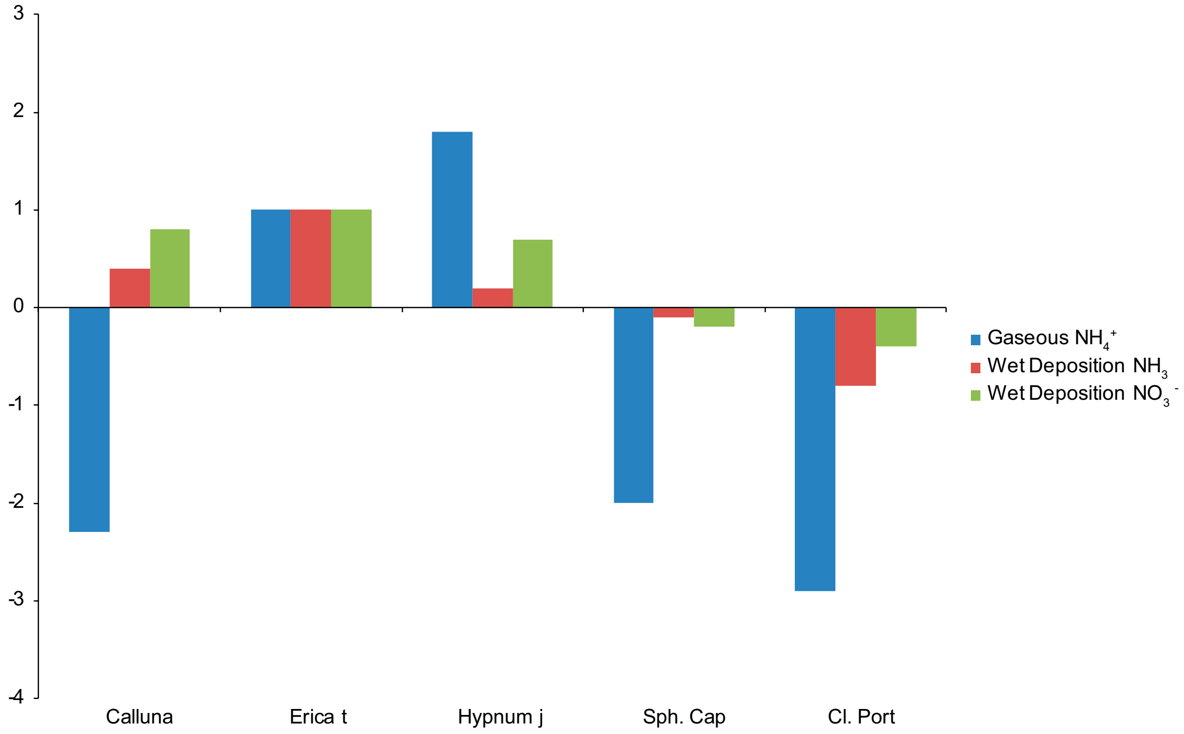


Figure 5.26: Proportional changes in the cover of key ericoids, *Calluna vulgaris* and *Erica tetralix*, mosses, *Hypnum jutlandicum* and *Sphagnum capillifolium* and the matt-forming lichen, *Cladonia portentosa,* in response to 5 years of 24 kg $ha^{-1}yr^{1}$ nitrogen deposition as ammonia, ammonium or nitrate, at the Whim experimental site (Sheppard *et al.*, 2009) (Values below the red line indicate loss of cover since 2002).

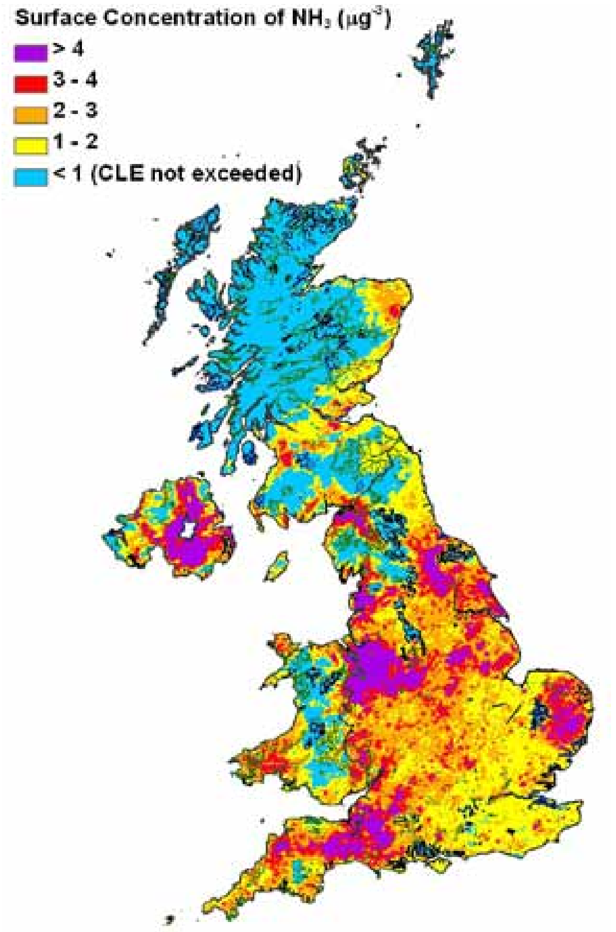


Figure 5.27: National map of ammonia concentrations for 2003, modelled by FRAME at 1 km resolution showing exceedance of critical levels. SAC and SPA boundaries are indicated by green and dark blue borders, respectively (some SACs are also SPAs, indicated by black borders).

The areas of the UK that are in exceedance of these two new critical levels are shown in Figure 5.27. The critical level of 1 μg m^{-3} is exceeded over 69% of 1k m squares in the UK, implying that adverse effects on the cover of sensitive bryophyte and lichen species may be expected over most of the country. The critical level of 3 μg m^{-3} for higher plants is exceeded over 19% of the UK, mainly in areas of high NH_3 emissions. These maps will in future need to be considered alongside those of critical load exceedance; they imply that policies need to focus on reducing emissions from major NH_3 sources to ensure that the adverse effects of N deposition on vegetation are reduced in the UK.

There remains the question of whether wet-deposited NH_4^+ and NO_3^- have different ecological effects. In the Whim experiment, the only major long-running UK experiment to provide such a comparison in the field, the vegetation has been treated with either ammonium chloride or sodium nitrate for over 6 years; there is no indication yet of an effect on species richness and no major changes in vegetation cover (Sheppard *et al.*, 2009), as were observed in response to gaseous ammonia. However, the N concentration of most vegetation types at Whim (ericoids, mosses and lichens) has increased significantly more with NH_4^+ than NO_3^- at the higher N loads, suggesting that any long-term effects, perhaps through interaction with other stresses such as drought, frost, pathogens or insects (Sheppard *et al.*, 2009), are more likely to be observed in response to reduced N. It is possible that these ions may have effects through different mechanisms – for example, direct toxicity from NH_4^+ but not NO_3^- ions in solution has been demonstrated in controlled experiments whereas NO_3^- may be more likely to enhance competition between species – but there is limited evidence from field studies.

There is evidence from national surveys that total reduced nitrogen (NH_x) deposition may be a more important driver of reductions in species richness and changes in species composition in semi-natural vegetation in the UK than total reactive nitrogen (NO_y)

deposition (Smart et al., 2003; Stevens *et al.*, 2006). However, these findings may reflect the greater range of deposition of NH_x than NO_y across the UK. Some studies have shown significant relationships between spatial or temporal patterns of vegetation change and NO_y deposition. For example, in a study of vegetation change in Scottish montane habitats, Helliwell and Britton (2010) concluded that across all community types total NO_y deposition was a more significant driver of species composition change than total NH_x deposition. Interpretation of survey data in terms of differential effects of the same rate of wet deposition in different chemical forms is problematic because of: (a) the generally similar spatial distribution of deposition of both oxidised and reduced forms; (b) the difficulty of separating the effects of gaseous NH_3 from those of wet-deposited NH_4^+; and (c) the fact that results are correlations rather than direct evidence of cause and effect.

In summary, gaseous NH_3 is much more likely than wet deposition to cause changes in vegetation for a given rate of N deposition, but no clear conclusions can be drawn on the relative effects of wet-deposited NH_4^+ and NO_3^-. It is likely that these different chemical forms will have different ecological effects via different mechanisms, which depend on soil conditions and vegetation composition, and hence a simple generalisation may not be possible.

5.4.7 Scientific basis of ozone risk assessment

Risk assessment for effects of ozone (O_3) on vegetation in the UK to date has primarily used the concept of the AOT40 index (Fuhrer *et al.*, 1997), which summarises the cumulative exposure to concentrations above 40ppb over the period of concern. The AOT40 index was also adopted for use in risk assessment by the CLRTAP and the EU. The AOT40 index introduces two key concepts – that effects of O_3 are primarily due to cumulative exposure above a threshold rather than acute episodes, and that there is a threshold concentration for significant effects to occur. Critical levels for O_3 using the AOT40 index have been derived for effects on annual arable crop yield, on forest growth, and on the growth and senescence of species of semi-natural vegetation. However, a number of limitations of this approach to risk assessment have been identified in recent years. Of particular relevance is a significant body of experimental research that has been supported by Defra over the past five years (CEH, 2010), and which has assessed the effects of relatively low O_3 exposures on species and communities of conservation value in the UK.

Firstly, as shown in Chapter 3, there has been a strong shift in the seasonality of O_3 exposure, reflecting the stronger influence of northern hemisphere background concentrations which peak in the spring. AOT40 index values at many rural sites are now as high in March as in June. This means that the use of a fixed seasonal AOT40 over the period May-July, as recommended by the EU, will provide a misleading picture of the risks of damage to UK vegetation. This also suggests that early season species (such as woodland bulb species, see Figure 5.28) are at an increasing risk of adverse effects.

Secondly, there is evidence that, over the last 20-30 years in the UK, peak concentrations of O_3 have fallen, while annual mean concentrations have increased (see Section 3.8). These trends are not captured by the AOT40 index, for which there is little significant trend, although the contribution of concentrations in the range 40-50 ppb to the seasonal cumulative AOT40 has increased relative to that of concentrations above 60 ppb, with mean concentrations now approaching and frequently exceeding 40 ppb in the UK. Hence there are important trends in the exposure of vegetation to O_3 across the UK which are not captured by use of the AOT40 index.

It is therefore important to understand whether these shifts in O_3 exposure patterns are significant for vegetation. Although experimental studies of the effects of O_3 have used a range of different exposure patterns, few have explicitly compared the effects of increasing peak concentrations with those of increasing background mean concentrations. In a series of experiments, Dawnay and Mills (2009) and Hayes *et al* (2010) exposed grassland species to background O_3 concentrations of 15-20 ppb and 35-40 ppb, each with or without added peaks of 50 ppb. In both studies, the low background with peaks induced the same amount of premature senescence as the high background without peaks even though AOT40 values were substantially different (e.g. 10.6 ppm.h for the low background plus peak treatment and 4.1 ppm.h for the high background treatment respectively for the Dawnay and Mills (2009) study).

A further very important finding from recent UK studies is that, when plants are exposed to a simulated increased background O_3 concentration (without added peaks) for 24h day^{-1} over one growing season, there is little evidence of any threshold for effects, and significant effects can be found when mean concentrations are increased from 20 ppb to 40-60 ppb. Figure 5.28 provides examples of these concentration–response experiments, showing effects on (a) competition between a forb and a grass species (b) stomatal conductance of a grass and forb species and (c) growth rate of three woodland bulb species. These represent a range of ecologically significant response variables. In addition, studies have shown that, of 13 grassland species exposed to O_3 for 20 weeks, 8 species had significantly greater senescence at 24h mean concentrations of 50 ppb and below than at the lowest treatment concentration of 20 ppb (CEH, 2010). All six woodland bulb species exposed to a range of 24h mean concentrations had a threshold for effects on bulb biomass below 40 ppb (CEH, 2010). Furthermore, there is important evidence for the cumulative effects of small simulated increases in background concentrations on above-ground biomass of a grassland community over a period of 5 years (Figure 5.29), suggesting that the effects of O_3 observed in studies over one growing season are indicative of gradually increasing effects over longer timescales (CEH, 2010).

These findings, using exposure regimes with no O_3 concentrations above 60 ppb and much of the exposure below 40 ppb, clearly demonstrate that the changes in O_3 exposure that are currently occurring in the UK could have a range of adverse ecological effects.

Finally, the AOT40 index is based on O_3 concentration immediately above the canopy. Since the primary sites of O_3 damage are within the plant, it has been argued that an index based on the cumulative stomatal flux into the leaves would provide a stronger mechanistic basis for risk assessment. This approach takes into account that locations or time periods with high O_3 concentrations may have reduced flux into the leaf because, for example, of high vapour pressure deficit or soil water deficit causing reductions in stomatal conductance. It is important to note that the effects that are described above would not be well captured by use of the AOT40 index, but would be captured by modelling of O_3 flux. This is because, under situations that are optimal for stomatal opening, critical flux thresholds could be exceeded with ambient concentrations well below 40 ppb (Danielsson *et al.*, 2003). This is illustrated clearly by recent data on effects on root growth of grasses under two watering regimes (Figure 5.30 (CEH, 2010)), which shows that differences in response to low O_3 exposures can be explained by the differences in cumulative modelled flux over the experimental period.

Definition of POD_Y-based critical levels

There is now a significant body of evidence, both statistical and biological, that an index based on the accumulated O_3 flux through the plant stomata (Phytotoxic Ozone Dose above a threshold of Y, POD_Y) is better related than AOT40 to well-recognised adverse effects of O_3 on crop yield and forest growth. For example, evidence of effects across Europe collated by Mills *et al.*, 2011, for the ICP Vegetation suggests that a flux-based evaluation is a better representation of the spatial distribution of impacts on vegetation across Europe than AOT40 (see Chapter 7 for more detailed information). Use of the

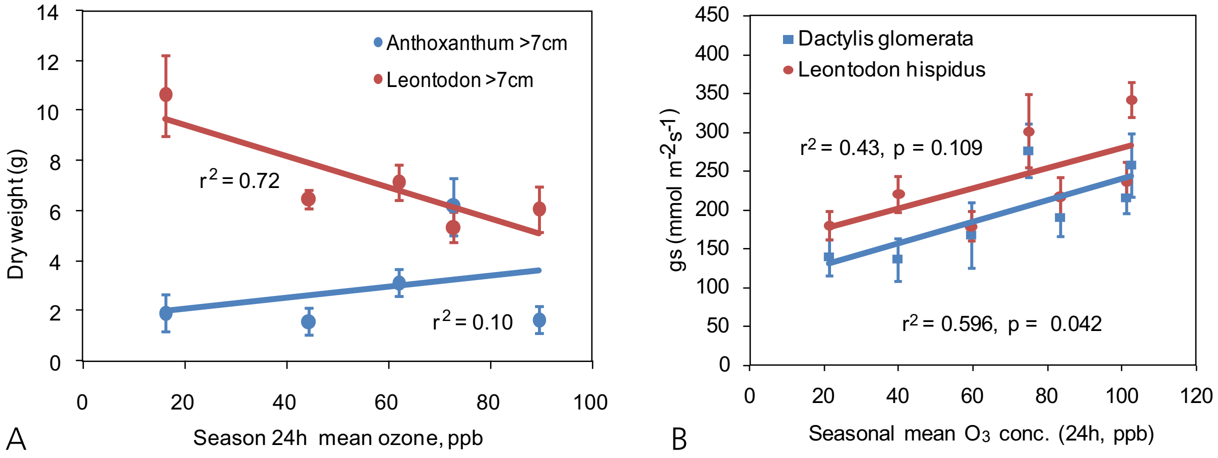
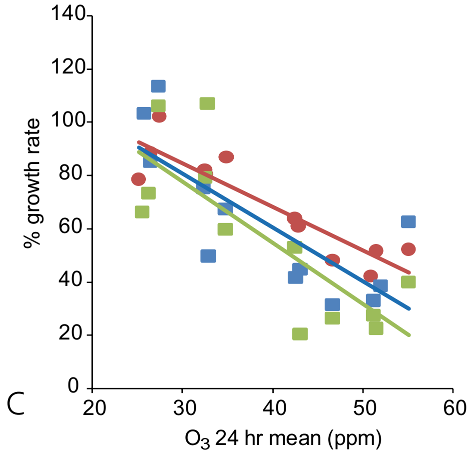


Figure 5.28: Examples of exposure–response relationships from recent UK studies, showing linear relationships with 24h mean concentrations of ozone. (a) Competition between a forb species *(Leontodon hispidus*) and a grass species (*Anthoxantum odoratum*), expressed as biomass of foliage above 7cm after exposure to ozone for 20 weeks in two growing seasons (CEH, 2010); (b) Stomatal conductance of *Dactylis glomerata* (open symbols) and *Leontodon hispidus* (closed symbols) (Mills *et al.*, 2009); (c) Growth rate relative to a 20 ppb threshold of the bulb component of three native spring bulb species: *Ornithogalum umbellatum* (red line; $R^2 = 0.83$, $P<0.001$), *Tulipa sylvestris* (blue line; $R^2=0.60$, $P<0.01$), *Frittilaria meleagris* (green line; $R^2=0.63$, $P<0.01$) (CEH, 2010).



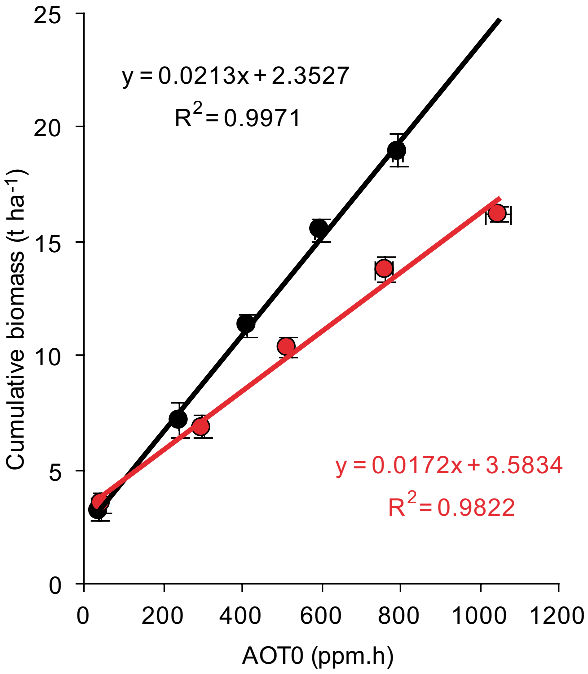


Figure 5.29: Impacts of simulated present day (black line; range of annual mean concentrations 20-24 ppb) compared with a simulated 2050 UK upland ozone climate (red line; range of annual mean concentrations 23-29 ppb) on the total cumulative above-ground biomass of a mesotrophic grassland community (CEH, 2010). The x axis shows the cumulative value of AOT40 in the two treatments in the five years from 2004 to 2008.

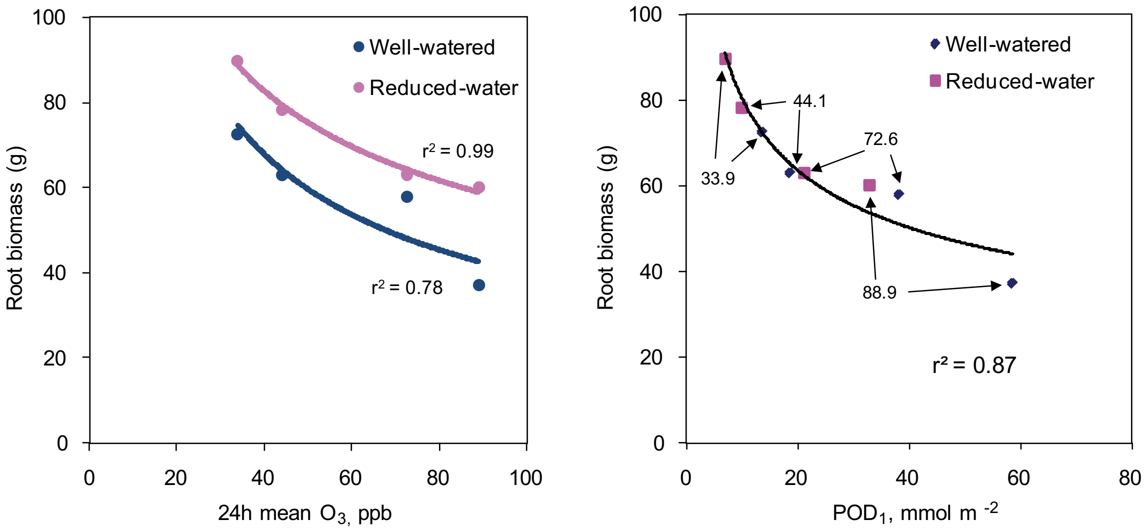


Figure 5.30: Effects on root biomass of the grass Dactylis glomerata either well watered or exposed to moderately reduced water supply after exposure for 20 weeks to increased background ozone concentrations (CEH, 2010). Responses under the two watering regimes can be explained by a single response curve. POD_Y calculated from a model developed from stomatal conductance measurements made during the ozone exposure period. The concentrations marked on the figure represent the seasonal 24h mean values for the indicated points.

POD_Y index (formerly known as $AF_{st}Y$) gives a very different spatial distribution of risk across Europe than does use of the AOT40 index (Simpson *et al.*, 2007, Mills *et al.,* 2011). Therefore, the use of POD_Y, rather than AOT40, can have significant policy implications.

In 2004, the CLRTAP formally approved the use of flux-based risk assessment at a European scale by including methods within the UNECE Mapping Manual (UNECE, 2004) and in 2008, the Executive Body of the CLRTAP recommended that flux-based risk assessment for vegetation should be used in the forthcoming revision of the Gothenburg Protocol. More recently, ICP Vegetation (Harmens *et al.*, 2010) led a systematic evaluation of the available evidence related to the POD_Y index. This has led to the recommendation of ten critical levels based on the POD_Y index, which are relevant to the UK. These are listed in Table 5.11. These critical levels were selected on the basis of the strength of the underlying dose–response relationships and to ensure that flux-based critical levels were available for the most important environmental effects of O_3 – on security of food supplies, carbon storage in forest trees, fodder quality of pasture and vitality of conservationally important ecosystems. These recommendations will be formally considered within CLRTAP during 2010. ICP Vegetation (Harmens *et al.*, 2010) also recommended the retention of AOT40-based critical levels for agricultural and horticultural crops, and forest trees, primarily because of concerns over the application of current flux-based methods in Mediterranean regions. These concerns are not relevant to UK evaluations.

Table 5.11: Flux-based critical levels for effects of ozone on vegetation, as recommended by Harmens e*t al* (2010) for use in CLRTAP (Note that there are different flux model parameterisations for each species. The POD parameter indicates the flux threshold Y used in the model. For each receptor, the effect is specified, along with the percentage change on which the critical level is based. The critical level derived from the flux–response relationship for that percentage change in the effect is listed, along with the actual critical level derived from the response function, and that recommended for use in mapping. The latter are the actual critical levels rounded up or down to the nearest integer value).

Receptor	Effect (% reduction)	Parameter	Critical level (actual) mmol m^{-2}	Critical level (Mapping Manual) mmol m^{-2}
Wheat	Grain yield (5%)	POD_6	1.2	1
Wheat	1000 grain weight (5%)	POD_6	1.2	1
Wheat	Protein yield (5%)	POD_6	1.8	2
Potato	Tuber yield (5%)	POD_6	3.9	4
Tomato	Fruit yield (5%)	POD_6	2.3	2
Norway spruce	Biomass (2%)	POD_1	8.2	8
Birch and beech	Biomass (4%)	POD_1	3.7	4
Productive grasslands (clover)	Biomass (10%)	POD_1	2.1	2
Conservation grasslands (clover)	Biomass (10%)	POD_1	2.1	2
Conservation grasslands (*Viola* spp.), provisional	Biomass (15%)	POD_1	6.3	6

Validation of models to predict POD_Y

For an assessment of whether these critical levels based on POD_Y are exceeded, it is important that the model used to derive flux–response relationships and POD_Y-based critical levels from experimental data is the same as that used to model geographical variation in the values of POD_Y. All the critical levels listed in Table 5.11 have been derived using the DO_3SE (Deposition of Ozone and Stomatal Exchange) model (Emberson *et al.*, 2001). DO_3SE is an ozone dry deposition model that can be combined with photochemical models to simulate both the total O_3 deposition to vegetated surfaces (for estimates of atmospheric O_3 mass balance) and the stomatal O_3 deposition (for estimates of O_3 risk (damage suffered by different vegetation types) using the POD_Y index). DO_3SE is currently applied at the European scale, as it is the dry deposition scheme used by the EMEP photochemical model. At the UK scale, work is underway to implement DO_3SE, and the specific parameterisations used to determine POD_Y-based critical levels, in both the Eulerian CMAQ model (run by Kings College London) and the Ozone Source–Receptor Model (OSRM) run by AEA Technology (for more details of OSRM, see Chapter 4).

The accuracy of simulations using DO_3SE is therefore an important issue in applying the POD_Y critical levels. These partly depend on the accuracy of the simulation of ozone concentrations by the photochemical model within which DO_3SE is embedded, which was discussed in Chapter 4. They also depend on the ability of the DO_3SE model to simulate O_3 flux from the O_3 concentration at a given height above the plant canopy, using relevant species-specific parameters which relate stomatal, and other conductances to O_3, to environmental conditions. Validation of the DO_3SE model has been performed using field measurements of O_3 flux and on other important components of the model (e.g. stomatal conductance and soil moisture deficit). The DO_3SE model has been evaluated across Europe in 11 studies at 12 locations for forest trees, in 5 studies at 5 locations for crops, and in 3 locations for 3 different community types for grasslands. These studies consistently show a high correlation, with limited bias, between modelled and observed data for stomatal conductance (the key parameter in modelling stomatal O_3 flux); modelling predictions are improved when local data are available for parameterisation (see for example, (Büker *et al.*, 2007; Nunn *et al.*, 2005; Tuovinen *et al.*, 2004)).

5.4.8 Assessment of current impacts of ozone in the UK

Both AOT40-based and POD_Y-based critical levels remain recommended for use in Europe, but the evidence from UK studies summarised above demonstrates clearly that the AOT40 index is no longer appropriate for assessment of the impacts of O_3 in the UK, especially given the changes in ozone exposure patterns that have occurred over the last 20 years. Furthermore, as described above, there is an accumulating body of recent evidence from UK studies that linear dose–response relationships with 24h mean concentrations can be derived under experimental conditions. Here we consider the implications of these findings for assessment of the current impacts of O_3 in the UK, considering in turn agriculture, forestry and biodiversity.

Where appropriate flux–response relationships exist, there is an increasing body of evidence that they provide an improved basis for risk assessment. However, to date POD_Y-based critical levels have only been developed for a limited range of species, and these values still require formal ratification for use within CLRTAP. Furthermore the new flux model parameterisations have not yet been incorporated into UK-scale photochemical models. Therefore, in this evaluation we present results for a limited number of the receptors listed in Table 5.11, based on EMEP-modelled O_3 concentrations and meteorological data supplied on a 50 x 50 km grid for a single year, 2000. Since the new flux-based critical levels listed in Table 5.11 have not yet been formally ratified for use within CLRTAP, we have used the current methods and paramaterisations in the UNECE Mapping Manual (UNECE, 2004). A full evaluation of the implications of the new POD_Y-based critical levels for assessment of the impacts of O_3 in the UK would require their application in UK-scale models for several years with different O_3 levels and meteorological conditions, but this was not possible over the timescale of this report.

Agricultural crops

The flux–response relationships that have been derived and approved for risk assessment within CLRTAP (UNECE, 2004) were used to estimate yield loss of wheat and potato in the UK in 2000. The flux-based yield–response relationships are described by Pleijel *et al.* (2007), and the relationships between AOT40 and yield loss are based on Mills *et al.* (2007).

Figure 5.31 provides, for wheat, mapped values of relative yield in the summer of 2000 based on (a) modelled POD_Y and (b) AOT40. For the POD_Y-based assessment, the yield losses range from 0% to 15%, with yield reductions over almost all of England being above 5%, and in many areas of East Anglia and southern Britain exceeding 10%. In contrast, for the AOT40 index, the predicted yield loss almost never exceeded 10% and in much of the UK was below 5%. Figure 5.32 provides the results obtained for potato in the same format. For both indices, the predicted yield losses were smaller, reflecting the lower sensitivity of this crop. While the yield losses based on AOT40 are below 2.5% almost everywhere in the UK, those based on POD_Y exceed 5% over significant areas of East Anglia and southern England. Hence for both these crops, substantially greater yield losses are predicted using the POD_Y index. Since it is now recognised, based on field evidence (e.g. Mills *et al.* (2011)), that only the POD_Y-based index should be used to quantify the effects of O_3, these are more reliable estimates of effects on yield than those based on AOT40.

The relative yield losses mapped in Figures 5.31 and 5.32 were combined with maps of crop area and production in order to quantify national crop losses. The area of the crop under cultivation in each grid square was estimated, and combined with an average national yield (in tonnes ha^{-1}) to estimate grid square-specific production and hence production losses, based on Food and Agriculture Organization (FAO) statistics[11]. The results obtained are shown in Figure 5.33. The greatest production loss for wheat is predicted to be in East Anglia, whereas for potato it is in south-west England and Northern Ireland. The overall national loss of production for wheat based on these data was about 1.2 million tonnes in 2000 (7% of national production); based on a 2000 market price[11] of £75 $tonne^{-1}$, this is equivalent to a loss of £90 million. The equivalent figure for potato is lower – a national loss of production of 140 thousand tonnes (2% of national production), equivalent to £12 million. There are many uncertainties in this

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[11] http://faostat.fao.org/

analysis, but it indicates the quite different estimates of impacts that are obtained using modelled POD_Y and AOT40, and the importance of the different spatial distribution of flux and crop production.

Holland *et al.* (2006) estimated yield losses for 23 arable and horticultural crops in 2000 across the EU based on the AOT40 dose-response relationships reported by Mills *et al.,* (2007). For the UK, the annual economic loss was estimated to be about £100 million. An earlier study (Holland *et al.*, 2002) showed that total UK financial losses due to O_3 effects on arable crops were almost all due to effects on five crops, split approximately as follows: 50% wheat, 25% potato, 10% sugar beet, 10% pulses and 5% oilseed rape. These estimates are broadly consistent with the analysis for this report, given that estimates using POD_Y will tend to be greater than those using AOT40. One limitation of the estimates for wheat yield loss has been that dose–response relationships are based on spring wheat, whereas UK planting is mainly of winter wheat. However, Gonzales-Fernandez *et al.* (2010) have demonstrated that effects on winter wheat are comparable to those on spring wheat; this study also showed that a group of sensitive cultivars had a yield loss twice that of a group of relatively resistant cultivars, suggesting that individual farmers could experience quite different yield losses from those estimated by generic species dose–response relationships.

These estimates do not include all the possible effects of O_3 on UK agriculture. Gonzales-Fernandez *et al.* (2010) reported that O_3 increased protein content and other determinants of grain quality, which would increase the value of the crop and partly offset any economic losses due to reduced yields; similar findings for European wheat were reported by Piikki *et al.* (2008). This is consistent with the lower POD_Y-based critical level for protein yield per hectare than for grain yield per hectare shown in Table 5.11.

None of these studies have included an estimate of effects on productive grasslands, although they cover a large area of the UK. In such grassland systems, economic impacts can be caused by changes in total productivity, forage quality, and species composition. Recently, Gonzalez *et al.* (2008) derived a flux–response relationship for forage yield and quality of grass:clover mixtures which could provide a basis for assessments of effects on grasslands. Ozone exposure significantly reduced clover productivity, nutritive quality and consumable food value (CFV), whilst there were no major effects on the nutritive quality or productivity of the grass. POD_Y was a better predictor of the effects of O_3 on the CFV than AOT40. These data, along with the new POD_Y-based critical level for productive grasslands based on clover yield (Table 5.11), provide the basis for extending economic estimates of O_3 impacts in the UK to include effects on improved grassland.

All these studies assume that exposure–response relationships derived from chamber experiments can be applied to farm-level production. Kaliakatsou *et al.* (2010) used an econometric approach to estimate the impact of O_3 using data for 66 cultivars of winter wheat at 149 trial plots over the period 1992-2004. The unbiased estimate of the elasticity of yields with respect to O_3 was 0.54% for a 10% increase in AOT40. At the mean value of AOT40 of about 3 ppm.h in their study, the yield loss for a 10% increase in AOT40 estimated from experimental data using the equation of Mills *et al.* (2007) would be about 1%. Hence estimates of yield loss based on field trial data would be about half those estimated using an AOT40 experimental model approach, which in turn are lower than those based on POD_Y, suggesting an overall difference of a factor of 3-4. This may be partly accounted for by unexplained variance in the econometric model, but it could also represent the effect of factors that operate at farm or trial level that are not considered in model estimates based on experimental studies. Kaliakatsou *et al.* (2010) suggest that one such factor may be the introduction of more ozone-tolerant cultivars; although other studies suggest modern wheat cultivars might be more ozone-sensitive (e.g. Pleijel *et al.*, (2006), there is little doubt that variation in sensitivity between cultivars is an important uncertainty in any estimate of national yield losses due to O_3.

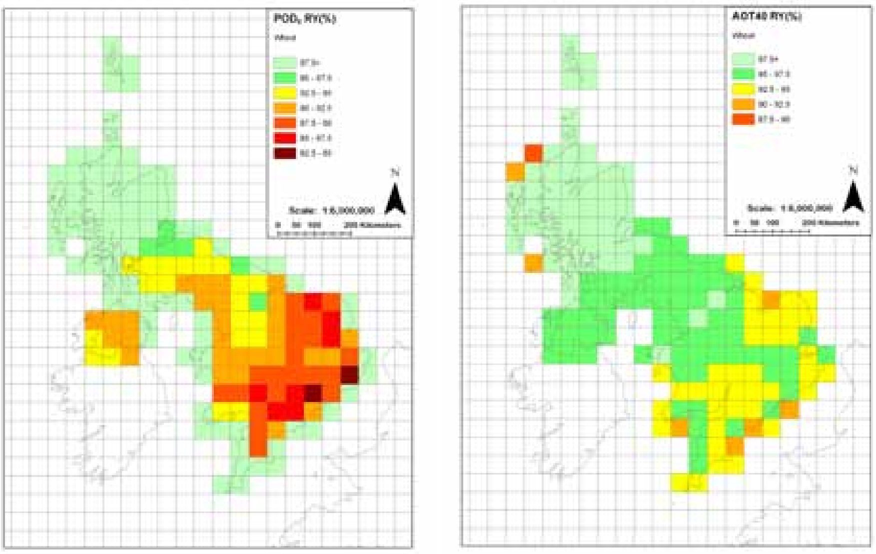

Figure 5.31: Estimated reduction in yield of wheat across the UK in 2000 using (a) POD_Y and (b) AOT40 All 50 km grid squares in the UK are shown, regardless of whether or not they contain wheat. RY% is the relative yield expressed as a percentage of that with no ozone exposure, i.e. a value of RY of 95% represents a 5% yield loss. For details of methods, see the text. These maps were produced for RoTAP by combining EMEP 50 x 50 km ozone and meteorological data for the year 2000 with receptor data from the SEI land cover map for Europe (UNECE, 2004). The DO_3SE model was used to estimate PODy according to formulations and parameterisations provided in the UNECE Mapping Manual (UNECE, 2004).

Forest trees

There is little recent experimental work in the UK to assess effects of O_3 on the growth of major tree species, although evidence summarised in NEGTAP (2001) demonstrates that ambient concentrations in the south of the country can have adverse effects on the growth of young trees. Re-analysis of experimental data has resulted in the definition of new POD_Y-based critical levels for the biomass of Norway spruce and the biomass of birch and beech (Table 5.10). However, since the model parameterisation described in the UNECE Mapping Manual (UNECE, 2004) only includes a critical level for birch and beech, we have mapped the modelled POD_Y for these species, using a flux threshold of 1.6 nmol m^{-2} s^{-1} (Karlsson *et al.*, 2007) rather than the value of 1.0 nmol m^{-2} s^{-1} that has been more recently recommended (Table 5.11). Figure 5.34 compares the results of this exercise to

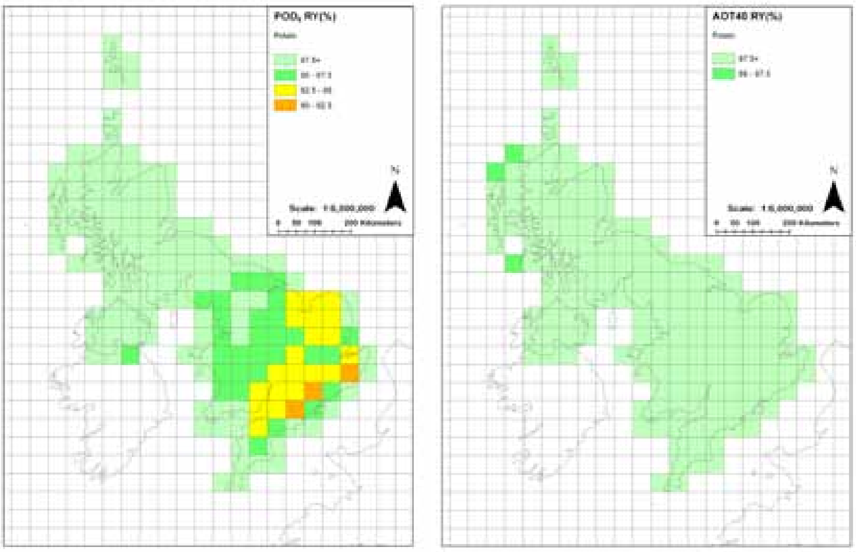

Figure 5.32: Estimated reduction in yield of potato across the UK in 2000 using (a) POD_Y and (b) AOT40. All 50 km grid squares in the UK are shown, regardless of whether or not they contain wheat. RY% is the relative yield expressed as a percentage of that with no ozone exposure, i.e. a value of RY of 95% represents a 5% yield loss. For details of methods, see the text. These maps were produced for RoTAP by combining EMEP 50 x 50 km ozone and meteorological data for the year 2000 with receptor data from the SEI land cover map for Europe (UNECE, 2004). The DO_3SE model was used to estimate PODy according to formulations and parameterisations provided in the UNECE Mapping Manual (UNECE, 2004).

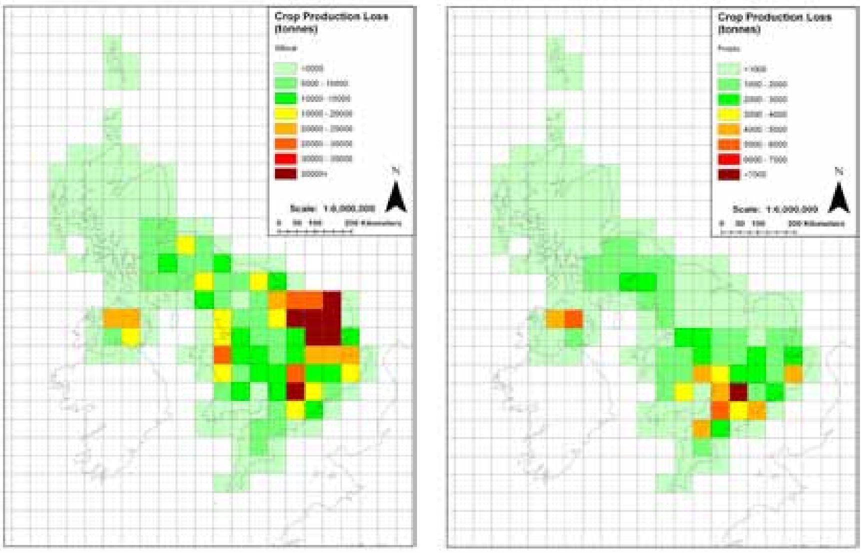

Figure 5.33: Modelled spatial distribution of production losses due to ozone across the UK in 2000 for (a) wheat and (b) potato. The plotted figures are the total loss of production (in tonnes) in each 50 km grid square. For details of methods, see the text. Maps were produced for RoTAP by combining EMEP 50 x 50 km ozone and meteorological data for the year 2000 with receptor data from the SEI land cover map for Europe (UNECE, 2004) and FAO production statistic data for the UK.

those obtained using AOT40. The results are expressed as RCL, the ratio of the modelled POD_Y or AOT40 to the critical level. Using the POD_Y index, the critical level is exceeded throughout the country, with significant parts of the country having modelled values of POD_Y that are over twice the critical level. This result is consistent with simulations using the OSRM flux model which predict that the POD_Y-based critical level for beech is exceeded throughout the UK (and also with the results reported by Simpson *et al.* (2007) using the EMEP model. In contrast, the AOT40-based critical level is exceeded over a small proportion of the UK land area only. Hence, as for wheat and potato, the adoption of the POD_Y index for risk assessment leads to increased areas and degrees of risk of adverse effects of O_3. The results show a gradient of increasing modelled POD_Y from north to south across the country, suggesting that species with a more southerly distribution, such as beech, may experience greater impacts on yield.

The level of exceedance of POD_Y-based critical levels may depend on the model parameterisation that is used. For example, undertaking the same mapping exercise using a parameterisation that has been specifically developed for Atlantic Central Europe led to greater values of RCL for beech. However, it is important to emphasise that the values mapped in Figure 5.34 do not include any effect of soil moisture deficit, and for a relatively drought-sensitive species such as beech, which often grows on thin soils, this may lead to a significant overestimate of the actual POD_Y. This factor is likely to be less significant for wheat, which is harvested relatively early in the summer season, or for potato, as it is assumed that soil moisture content would be maintained above a critical threshold through irrigation.

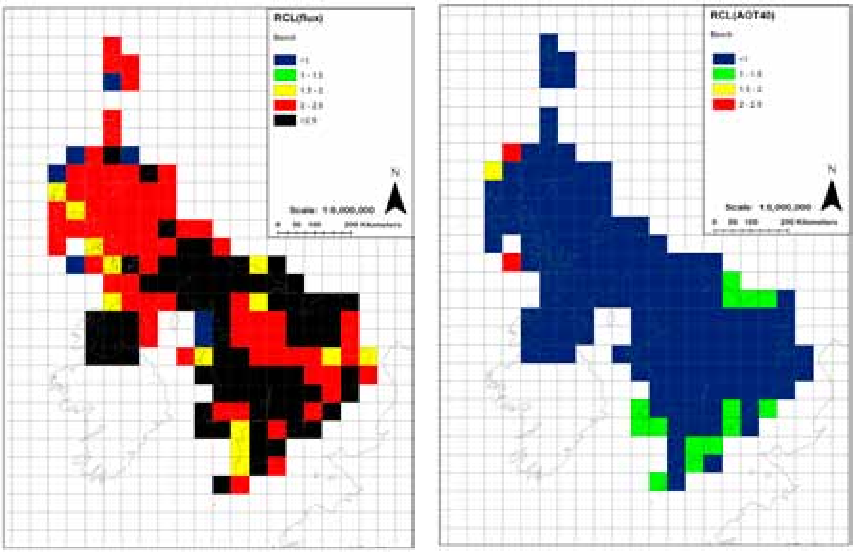

Figure 5.34: Modelled spatial distribution of (a) POD_Y and (b) AOT40 for beech in 2000. In each case, the modelled values are expressed as a value relative to the critical level (RCL), where RCL is the ratio of the modelled POD_Y or AOT40 to the critical level. For details of the method, see the text. Maps were produced for RoTAP by combining EMEP 50 x 50 km ozone and meteorological data for the year 2000 with receptor data from the SEI land cover map for Europe (UNECE 2004). The DO_3SE model was used to estimate PODy according to formulations and parameterisations provided in the UNECE Mapping Manual (UNECE, 2004).

Effects on biodiversity

Much of the recent experimental work in the UK has focused on semi-natural plant communities. The diversity of such communities, and the limited data available, make a detailed assessment of the national implications of these findings problematic. Most of the assessment of evidence provided here is based on AOT40 or 24h mean ozone concentration, with the latter indicating effects of increasing background ozone concentration. New POD_Y-based critical levels have been derived very recently for an indicator species of grasslands, and for clover biomass (see Table 5.11). However, since we have based our evaluation for this report on the methods described by the UNECE Mapping Manual (UNECE, 2004) which did not include POD_Y-based critical levels, it is too early to make an assessment of the extent to which these new POD_Y-based critical levels are exceeded in the UK.

While the evidence base is too limited to provide clear conclusions on where O_3 may pose the greatest threat to achieving targets for protection of biodiversity, there is an accumulating body of evidence that O_3 could have significant adverse effects on communities of high conservation value. Morrissey *et al.* (2007) identified Biodiversity Action Plan (BAP) Priority Habitats at greatest risk from O_3 based on the proportion of their distribution over which the critical level for O_3 effects, expressed as an AOT40 value, is exceeded, and the evidence of adverse effects on key indicator species based primarily on relative sensitivities provided by Hayes *et al.* (2007a). Morrissey *et al.* (2007) concluded that there was little evidence of adverse effects of season-long exposure to O_3 on key species of montane, coastal wetland and heathland habitats, although these did show sensitivity in a European assessment (Mills *et al.*, 2007), but there was such evidence for UK woodland and grassland habitats. The information for these latter habitats has been updated since the study of Morrissey *et al.* (2007) and is summarised in Table 5.12. For all four of the habitats in Table 5.12, the AOT40-based critical level for adverse effects of O_3 on communities dominated by perennial species (an AOT40 of 5 ppm.h accumulated over 6 months) is exceeded over a significant proportion of the UK area of the habitat, and there is experimental evidence to demonstrate that O_3, at relatively low concentrations, can have effects that would reduce the conservation value of the habitat. However, unlike N deposition, no spatial surveys exist to assess if species richness or species composition is different in areas of the country with higher O_3 concentrations; this partly reflects the relatively small spatial gradients in O_3 across the countryside and partly the difficulty of defining appropriate O_3 exposure metrics.

Several of the key studies used in constructing Table 5.12 have consisted of exposure–response relationships based on 24h mean exposure during the growing season, which have shown biologically significant effects of exposure to a 24h mean concentration in the range 35-50 ppb compared with 24h mean exposure in the range 25-30 ppb. Figure 5.35 shows the distribution of mean concentrations over the periods March-May (for comparison with woodland bulb data) and May-July (for comparison with grassland species data), averaged over the period 2003-07. A 24h mean concentration of 35 ppb is exceeded over significant areas of the country in the March-May period when the northern hemispheric background concentration is its highest, including over the northern half of Scotland, upland Wales and northern England, and parts of southern and eastern England. In contrast, the area with mean concentrations above 35 ppb is smaller in May-July, covering parts of south-east England and some upland areas of Wales and northern Scotland. These results, taken with the results in Figures 5.31-5.34, suggest that northern hemisphere background concentrations of O_3 have now increased to a level where they may have adverse effects on sensitive species during spring in some parts of the UK.

Table 5.12: Summary of potential impacts of ozone on habitats of major conservation importance (The second column provides estimates of the proportion of the UK which is in exceedance of the critical level of an AOT40 of 5 ppm.h over six months (April-September). Adapted from Morrissey *et al.* (2007) to include new data as indicated in references.

Habitat	% of UK area of habitat above critical level	Observed adverse effects of ozone	References
Calcareous grassland	71.5%	Reduced cover of dominant fine grass species and characteristic forb species	Thwaites *et al.* (2006)
Acid grassland	25.9%	Decreased cover of characteristic grass species and forbs	Hayes *et al* (2010)
Mesotrophic grassland	21.8%	Reduced total productivity, reduced cover of dominant fine grass species, and reduced cover of legume species Decreased cover of forbs, increased grass cover	CEH (2010)
Deciduous woodland	57.3%	Reduced flowering and bulb growth in characteristic woodland ground flora species Increased cover of shade intolerant woodland species	CEH (2010) Keelan (2007)

5.4.9 Combined effects of ozone and nitrogen deposition

Thus far, we have considered the effects of O_3 and N deposition in isolation. Given the large areas of the UK that exceed critical levels of O_3 and critical loads for N deposition, the nature of their combined effects is important. In terms of ecological effects in grassland ecosystems, for example, both O_3 and N deposition tend to reduce the proportion of legumes and forbs and favour dominance by aggressive grass species. A number of mechanisms exist for interactive effects and the adverse effects of O_3 have been reported to be both increased by increased N supply (e.g. (Utriainen and Holopainen, 2001) and decreased by increased N supply (e.g. (Jones *et al.*, 2010; Whitfield et al., 1998). The one large-scale field experiment which aims to quantify these effects in grasslands has to date shown no significant interactions (Bassin *et al.*, 2009).

A further major uncertainty in assessing the implications of atmospheric deposition for biodiversity in the UK is that studies have almost exclusively focused on plant species. Changes in plant species composition would be expected to have implications for a range of invertebrate taxa, and there is clear evidence that changes in plant chemistry induced by ozone and N deposition can affect insect performance. For example, in a long-term

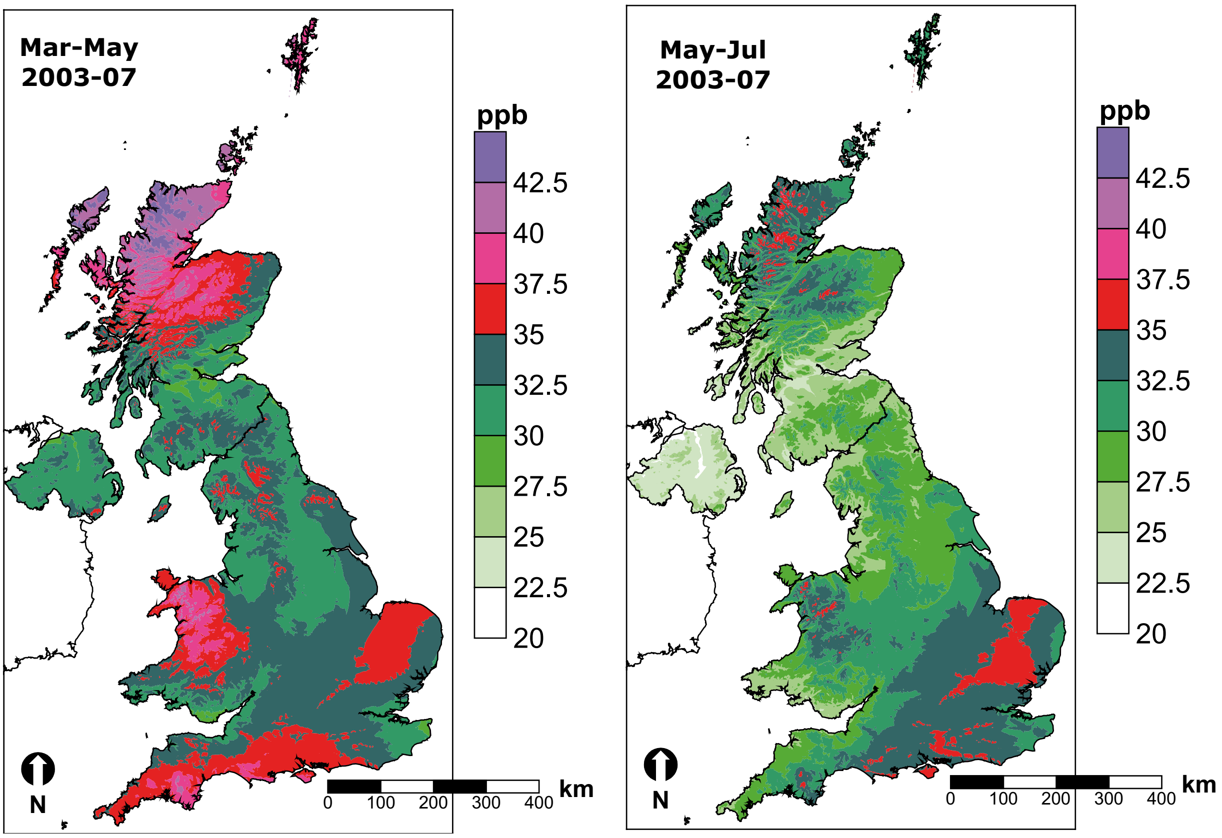

Figure 5.35: Distribution of mean ozone concentrations over the periods March-May (for comparison with woodland bulb data) and May-July (for comparison with grassland species data), using data for the five year period 2003-07 (Coyle *et al.*, 2002).

field experiment in the US, Haddad *et al.* (2000) reported that a decrease in insect species richness was associated with decreased plant species richness in response to simulated N deposition, although different groups of insects showed positive and negative responses to N deposition.

5.5 Common themes in effects on waters, soils and vegetation

This chapter has considered the effects of deposition on soils, waters and vegetation largely in isolation. In these final sections, we identify and discuss a number of common themes which are relevant to all three types of impacts.

5.5.1 Biological indicators of pollution impacts

Bioindicators are important tools for identifying the health of an ecosystem or habitat in relation to pollutant exposure, and are central to the assessment of ecological status under the Water Framework Directive. There is much demand from those concerned with impacts at the habitat scale for reliable and simple techniques to reveal both the level of pollutant deposition and any resulting ecological impact. Similar information is required over regions to confirm predictions of exceedance of pollutant thresholds such as critical loads and levels. There is a long history of biological indicator development with respect to freshwater acidification. Palaeoecological indicators (e.g. diatoms) have been developed to inform on past changes in the acidity of lakes and provide future recovery targets (e.g. Battarbee *et al.*, 2005), while the specific sensitivity of acid-sensitive species, and particularly salmonids, forms the basis for the determination of critical levels for freshwater acidity (Lien *et al.*, 1996). Comprehensive reviews of the various types of N pollution bioindicators suitable for terrestrial sites were produced by Sutton *et al.* (2004) and methods were further examined by Leith *et al.* (2005), Morecroft *et al.* (2005) and Stevens *et al.* (2009).

A combination of research using long-term field N addition experiments and surveys along local or regional pollutant gradients have generated valuable potential indicators. Table 5.13 provides an overview of important indicators for N deposition in vegetation, soils and waters, focusing on those referred to in this report, and identifying key strengths and weaknesses. Increasing exposure to N pollution is likely to initially cause N accumulation within components of the terrestrial system followed by biogeochemical change potentially leading to alteration of ecological structure and/or function in the terrestrial and the receiving aquatic environment. Along this 'biomonitoring chain' (Leith *et al.*, 2005), methods have been used to provide information at different stages, from pollution exposure (e.g. using N content of mosses (Pitcairn *et al.*, 2006)), to physiological and functional changes (e.g. changes in plant phosphatase activity and chlorophyll fluorescence (Arroniz-Crespo *et al.*, 2008) or changes from N to P limitation of productivity in lake phytoplankton (Maberly *et al.,* (2002), to ecological consequences (e.g. alteration of lichen community structure (Wolseley *et al.*, 2004) or overall loss of plant diversity (Stevens *et al.*, 2006)).

It is difficult, however, to recommend ideal indicators of pollution exposure or ecological change across varied habitats that reliably and consistently indicate excess N deposition. For example: accumulation of N in plant tissues or soils is not always seen along N pollution gradients (Stevens *et al.*, 2006); epiphytic tree lichens are not present in many habitats; and increasing N deposition is not always linked to an elevated Ellenberg N plant score (Leith *et al.*, 2005; Stevens *et al.*, 2006). Several responses to N could also be caused by other environmental influences. It is unlikely, therefore, that a single indicator would be sufficient to indicate change resulting from pollutant exposure. The most reliable approach would need to be tested for each habitat type, but is likely to require a combination of: (a) measures of N accumulation; and (b) observations of significant ecological effects. Furthermore, attribution of changes to pollutant exposure will be possible through an understanding of the pollution environment gained by atmospheric monitoring or dispersion modelling, and knowledge of a potential local or regional emission source.

Table 5.13: Examples of indicators for nitrogen deposition in soils waters and vegetation.

Indicator	Good points	Weak points	Examples
Biogeochemical: N accumulation			
Plant total % N	Standard assay, widely studied, often correlated to N deposition	Not always related to N deposition; indicates recent N enrichment	(Pitcairn *et al.*, 2006) See Sections 5.4.2 and 5.4.3
Plant-soluble NH_4^+	More sensitive than total N to N deposition	May be influenced by other conditions or reflect recent N exposure	(Leith *et al.*, 2005)
Soil or litter total % N	Indicates long-term soil N accumulation and potential for nitrate leaching	Not always related to N deposition	See Section 5.2.2
Exchangeable soil NH_4^+	Can show marked positive responses to N supply	Highly dependent on season, weather, etc.	(Edmondson, 2007) See Section 5.2.2
Nitrate as a proportion of total nitrogen (TN)	Easy to measure and robust indicator of influence of N deposition on upland waters	Can be influenced by local point source inputs	This report
Biogeochemical: Effects			
Soil and plant phosphatase	Shows consistent positive responses to N supply in a range of habitats	Variable response in field surveys, influenced by ecosystem P status	(Arroniz-Crespo *et al.*, 2008); (Pilkington *et al.*, 2005)
Inorganic N leaching	Shows responses to N supply in varied ecosystem field experiments	Differs between ecosystems as some accumulate more N	(UKREATE experiments and surveys) (UKREATE, 2010) See Section 5.2.2
Potential soil N net mineralisation	Large responses to N in field experiments and Countryside Survey	Influenced by seasonal and weather conditions	See Section 5.2.2
N saturation stage	Indicates degree to which aquatic catchment soils are able to retain N deposition	Can be influenced by local point source inputs	(Stoddard, 1994)
Ecological change			
Single species	Several known low and high fertility-indicating species are known	Few reliable indicator species of N as opposed to general fertility	(Grime *et al.*, 1988)
Ellenberg N plant score	Well-used indicator of fertility, sometimes correlating with N deposition	Reflects fertile soils, not just N supply	(Smart et al., 2003)
Epithytic lichens	Assemblages of lichens correlate well with N exposure	Influenced by other inputs; epiphytic lichens absent from many habitats	(Leith *et al.*, 2005; Wolseley *et al.*, 2004)
Aquatic macrophytes	Some oligotrophic species are highly sensitive to elevated nitrate levels	Substrate and other physico-chemical factors also influential	(Roelofs, 1983)
Aquatic algae	Bioassays used to assess N limitation of algal productivity	Relatively labour intensive	(Maberly *et al.*, 2002)

5.5.2 Effects of management and the potential for mitigation

Afforestation and forest management

Historically, the enhanced aerodynamic roughness of forest canopies (Fowler *et al.*, 1989; Mayer and Ulrich, 1977) has resulted in higher acid loads to forested catchments in comparison with neighbouring moorland. Reynolds *et al.* (1995) demonstrated that sodium (Na^+), chloride (Cl^-), sulphate (SO_4^{2+}), nitrate (NO_3^-), aluminium (Al) and hydrogen ion (H^+) output fluxes from upland catchments in Wales were all enhanced by forestry, while a palaeoecological assessment of adjacent AWMN sites demonstrated earlier and more rapid acidification in the forested Loch Chon than moorland Loch Tinker (Kreiser *et al.*, 1990). In acid-sensitive catchments commercial plantation forestry may also lower long-term soil-buffering potential as a result of base cation uptake into the crop and subsequent removal by harvesting. The magnitude of this effect is crucially dependent on harvesting regime, being more acute when some form of whole tree harvesting is practised (Reynolds and Stevens, 1998). Furthermore, as forests reach maturity and growth rates decline, the supply of N from atmospheric deposition may exceed the biological demands of the forest ecosystem. The excess nitrogen is leached as NO_3^- in run-off thereby increasing the acid inputs to receiving waters (Emmett *et al.*, 1993).

Harriman *et al.* (2001) showed that trends in S and N concentrations in uplands between 1977 and 2000 in four areas across Scotland were dependent on the use of the land and the stage in the forest cycle. Particularly large reductions in xSO_4^{2-} occurred in recently felled catchments (removal of forest canopy). Nitrate concentrations increased at sites felled late in the study, but decreased at sites where felling occurred early, and particularly at sites where second generation forest was becoming established. Alkalinity and pH increased in moorland and felled areas but changed little at sites where forests were aggrading. Harvesting is often accompanied by a short-term increase in NO_3^- leaching (and associated temporary acidification) which may last between three and five years (e.g. (Tetzlaff *et al.*, 2007)). Effects are seen most clearly where a large proportion of a catchment is felled in a short time (Neal *et al.*, 1998). Published guidelines now take this into account so that in acid-sensitive areas the area of forest felled concurrently within a catchment may be limited depending on the outcome of a site-specific assessment (Forestry Commision, 2003).

Most AWMN forested sites (i.e. Afon Hafren, Llyn Cwm Mynach and Loch Grannoch) show less evidence of chemical or biological recovery than moorland sites. These sites tend to be more acidified than nearby moorland AWMN site equivalents and recovery to date has been dominated by reductions in inorganic aluminium (Al_i) concentrations rather than pH increases. At Llyn Brianne the mean H^+ concentration in acid forest streams has declined by 8-15 μeq l^{-1} over the last 25 years but mean winter pH increased by only 0.4 units and has remained too acid for invertebrate recolonisation (mean pH 4.8-5.2; Al > 0.3-0.6 mg l^{-1}), particularly during episodes.

Heathland management

The effects of management are incorporated into the calculation of mass-balance critical loads if nitrogen and base cations are exported from the site through fire, grazing and/or harvesting. Removal of N effectively increases the critical load for N whilst removal of base cations decreases the critical load for acidity. A large amount of work has been reported describing the increased risk of acidification due to effects of afforestation on acid-sensitive soils due to removal of base cations in harvested wood but effects of management in other habitats are poorly quantified. Assumptions about this export from the site can have significant impacts on critical load calculations. For example, N losses through fire have been incorporated into the critical load calculations for dwarf shrub heath, with a value of 4.5 kg N ha^{-1} yr^{1} applied to all areas of wet heaths and a value of 10 kg N ha^{-1} yr^{1} applied to all areas of dry heath. These removal rates are based on studies published by Power *et al.* (2004) and Terry *et al.* (2004). However, this approach assumes that all areas of heathland mapped in the UK are subject to burning, resulting in an overestimate of the critical load values for areas of heathland where burning does not occur, for example in many parts of Wales where grazing is the primary management practice.

If N removal by burning is excluded from the critical load calculations it is estimated that 65% of the habitat in the UK will have exceedance of acidity critical loads based on acid deposition for 2003-05. Including the effect of burning, using the removal rates above, reduces the habitat area exceeded to 42% using 2003-05 deposition. Some form of management and biomass removal must always be in place in order to prevent heathlands degrading or undergoing succession to woodland, but this is not well-mapped at present. Further work to quantify the impacts of management for heathlands, in particular N removal rates by burning and the extent of heathland burning across the UK would improve our critical load (and exceedance) estimates for this habitat. Similarly, site-specific applications must modify this parameter for any habitat to ensure appropriate critical load and exceedance calculations. A recognition of the combined risk of management and air pollution for soil acidification is currently under consideration as one of the major threats to soils at a European scale to be incorporated in a new EU Soils Framework Directive.

Management as a mitigation tool

Can management be used as a mitigation tool for air pollution impacts? This approach should be used with caution as most management options have a wide range of physical, chemical and biological impacts. A full assessment of likely impacts on all features of interest or ecosystem services should be assessed before any management option is implemented. For example: (i) increased intensity of grazing to remove nitrogen to below the critical load threshold for a site may be equally damaging to vegetation through direct effects of trampling, while the soil carbon stock could be threatened by any associated increase in erosion; (ii) increased removal of wood biomass to remove nitrogen will export base cations thus increasing the risk of acidification; and (iii) increased frequency of fire to rejuvenate heather where nitrogen has accelerated succession may affect other biota and could again physically destabilise the soil.

The efficacy of management also needs consideration. More intense management to increase rates of N removal could also play a role for actively managed habitats such as grasslands and heathlands, but the experimental evidence suggests that management can only have a limited effect in mitigating the adverse effects of N deposition (e.g. (Plassmann *et al.*, 2009; Power *et al.*, 2006). In heathlands and grasslands, recovery of the original vascular plant species diversity may only be possible with active management intervention. In the Netherlands, for example, where large reductions in NH_4^+ deposition have been achieved in some areas, soil conditions still prevent the establishment of sensitive heathland and acid grassland species and active management by nutrient removal and lime application is first needed to restore the necessary geochemical conditions (Kleijn *et al.*, 2008).

5.5.3 Effects of climate change

The potential effects of climate change on air pollution impacts on soils and vegetation are potentially very wide-ranging and include: (i) changes in the tolerances of plant species to soil acidification and N enrichment under different climate conditions; (ii) increased frequency of climatic stresses to which air pollution increases sensitivity (e.g. drought); and (iii) increased uptake, weathering and leaching of N and base cations and increased base cation weathering due to climate-induced changes in plant growth and hydrological conditions. Other potential climate change interactions, for example through increased frequency of pest and pathogen outbreaks to which air pollution has increased sensitivity, are not considered here.

Research to quantify climate change effects mediated directly or indirectly through the soil includes a number of different aspects. Modelling work on ecological niches for more than 1000 higher plants under different climate conditions in combination with changes in soil conditions and management will allow the definition of different tolerance levels of plants with respect to soil acidity and nitrogen enrichment under different climate and management conditions (Smart *et al.*, 2010). Experimental approaches simulating the effects of repeated summer drought or warming on soils and vegetation is ongoing in a range of habitats across the UK including upland heathland/moorland systems (Sowerby *et al.*, 2008; UKREATE, 2008), calcareous and mesotrophic grassland, and montane systems. Results to date suggest relatively small changes in soil acidity and nitrogen fluxes (Sowerby *et al.*, 2010). Instead, changes in ecosystem functioning were dominated by changes in soil carbon dynamics and the water-holding capacity of the soil.

The impacts of climate change on the sensitivity of European forest ecosystems to S and N deposition due to changes in soil and forest nutritional status have been studied under the EU-funded project AIR-CLIM (Alacamo *et al.*, 2002; Mayerhofer *et al.*, 2001; Posch, 2002). One aspect of the project examined the impacts of eight climate scenarios on the calculations of critical loads, deposition and exceedances. Changes in temperature influence soil base cation weathering rates while changes in precipitation affect run-off (precipitation surplus) and the leaching of base cations and nitrogen, and both may influence tree/vegetation growth determining nutrient uptake rates. The AIR-CLIM study, based on a uniform European-scale database, demonstrated for all scenarios a general increase in critical loads for forest soils across Europe, though with some decreases to values in mountainous or arid regions. It also showed a decline in the area exceeded for all scenarios, leaving only small areas with exceedance for acidity, but substantial areas exceeded for N. However, Posch (2002) emphasised that (a) achieving non-exceedance of acidity critical loads does not imply immediate recovery of ecosystems previously exceeded; and (b) higher resolution deposition data would give more widespread exceedance of critical loads.

Work focused on the potential implications of climate change for UK forests also suggests only small changes in the uptake and removal of base cations and nutrients will occur in response to climate change scenarios, elevated carbon dioxide (CO_2) levels and management scenarios (Sowerby *et al.*, 2010). Baseline uptake values of 0.161 keq ha^{-1} yr^{1} for calcium, 0.252 keq ha^{-1} yr^{1} for base cations and 0.16 keq ha^{-1} yr^{1} for N, only increase to 0.194, 0.31 and 0.205 respectively. The method used to calculate acidity critical loads is relatively insensitive to such small changes in calcium uptake values, and hence the area of managed conifers with critical load exceedance only increases by 1% from the baseline scenario (i.e. 71% compared to 70% with the baseline). The method is most sensitive to changes in calcium and base cation weathering rates and total calcium deposition. Likewise for N, the method for calculating nutrient N critical loads for managed conifers is more sensitive to N uptake and N leaching than to N immobilisation or denitrification. Due to the small difference in the N uptake values between the baseline and the ‘climate change + management’ scenario, the impact on critical loads is small, leading to just a 1.5% decrease in the area exceeded for nutrient N under the scenario. The uptake values used here were applied to all areas of managed coniferous woodland across the UK; it is likely the values will vary regionally due to climate and species type and a more detailed analysis may produce different results, particularly for N uptake which plays a larger role in determining the eutrophication critical load. However, the results suggest that changes in plant growth may not be a major source of change to critical loads under a changing climate.

In terms of effects on waters, climate change can be expected to have long-term effects on the fundamental catchment processes that determine susceptibility to acidification and NO_3^- leaching. In well-buffered catchments, higher temperatures may boost alkalinity by increasing weathering (Sommaruga-Wögrath *et al.*, 1997) but this effect is expected to be small in poorly buffered catchments (Wright and Dillon, 2008). Warming in the absence of other stresses can be expected to accelerate biological activity in general, including plant productivity, soil respiration and N mineralisation (Rustad *et al.*, 2001). The net impact will depend on site attributes including vegetation type, soil C pool, N availability and moisture status (Shaver *et al.*, 2000), but potential consequences might include increased NO_3^- and DOC leaching (Clark *et al.*, 2009; Wright and Jenkins, 2001). Long-term loss of soil organic matter would also reduce soil capacity to immobilise and store deposition inputs. However, concurrent changes in soil moisture status could significantly confound ecosystem responses to warming due to the interacting effects of temperature and moisture on biological processes; decomposition may become moisture-limited under dry conditions, but oxygen-limited under very wet conditions, as in peats (e.g. (Emmett *et al.*, 2004; Toberman *et al.*, 2008). Increased incidence of drought in drier summers, or waterlogging during wetter winters, could thus offset the effects of increased temperatures such that (given also the uncertainty in General Circulation Models (GCM) predictions of rainfall change) the overall effects of climate change on long-term NO_3^-, DOC and acidity levels are difficult to predict.

As well as influencing long-term biogeochemical cycles, climate is important with regard to determining the frequency, intensity and seasonal timing of extreme events, such as acidic episodes in streams. Although most surface waters are now recovering from acidification, many remain susceptible to acid episodes, due to the legacy of base cation depletion and pollutant accumulation in soils. Acid episodes are invariably associated with climatic extremes, i.e. high flow, sea-salt events, freeze-thaw and drought; any increase in their frequency and/or intensity would raise the risk of biologically harmful events, and impede biological recovery.

An additional significant factor for vegetation is how climate change will modify the effects of O_3. Chapter 4 provides OSRM scenarios for 2020 based on flux metrics, showing that the extent to which O_3 flux in the UK will be reduced in the future depends critically on trends in northern hemisphere background concentrations. Any evaluation of the significance of recent and future trends for O_3 impacts on vegetation needs to consider the projections in the context of possible changes in climate. Detailed mechanistic modelling would be needed to assess the implications of the different interactions. Here we emphasise two key interactive factors.

The first of these is water availability. UK Climate Impacts Programme (UKCIP) scenarios suggest a trend to hotter drier summers in the UK (Hulme *et al.*, 2002). Simple application of flux-based models would imply that this would reduce the impacts of O_3, due to the reduced flux of O_3 through the stomata, especially for species with growth in mid- and late summer when soil moisture deficit will be greatest. However, new evidence has demonstrated, using UK grassland species, that O_3 exposure interferes with hormonal signalling to prevent the normal closure of stomata in response to soil drying (Mills *et al.*, 2009; Wilkinson and Davies, 2009). Importantly, this effect has been found in apparently healthy leaves at 24h mean concentrations close to those already found in the UK, with a threshold for statistical significance of about 55 ppb. The implications of these findings for seasonal cumulative O_3 flux, and effects on vegetation, need further investigation.

The second is carbon dioxide concentrations. There is an extensive literature on interactions between CO_2 and O_3 which suggests that elevated CO_2 concentrations reduce O_3 impacts. A possible scenario for the turn of this century is that atmospheric CO_2 and O_3 concentrations will have increased, while summer rainfall will have greatly reduced. The only experiment to address the interactive effects of these factors on the responses of commonly planted tree species in lowland England (Broadmeadow and Jackson, 2000) showed that oak was the most responsive species to all treatments; while elevated CO_2 and irrigation increased biomass by 79% and 41% respectively, O_3 reduced growth by 30%. Ozone increased branching which resulted in changes to allometric relationships. Elevated CO_2 provided some protection against O_3 effects, especially with limited soil moisture availability. These interactions between CO_2, O_3 and water supply must be taken into account when predicting the effects of environmental change on tree growth and forest productivity, as well as agricultural production and the composition of semi-natural communities.

5.5.4 Effects of air pollution on greenhouse gas fluxes

In addition to the possible impacts of climate change on the environmental impacts of air pollution it is also important to consider how air pollution effects may feed back to the climate system through the modification of greenhouse gas fluxes in soils and vegetation.

In terms of soils, the rate of N deposition can significantly influence soil C and N cycles and consequently the production and consumption of the greenhouse gases carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4) and the tropospheric ozone precursor nitric oxide (NO) in natural ecosystems. The initial response to enhanced deposition rates, as simulated by experiments, is very different to the responses observed in long-term N addition field experiments or by comparing common ecosystems along atmospheric N deposition gradients. Pristine forests and moorlands in areas of low N deposition rates tend to be N-limited and the first episodes of enhanced N deposition (as simulated by short-term field experiments) will stimulate microbial activity and increase soil respiration rates and consequently CO_2 emissions (Bowden *et al.*, 2004). Nitrous oxide emissions are unlikely to be affected, as the N added is immobilised by the microbial community (Skiba *et al.*, 1999). However, continuous N deposition will eventually lead to N saturation, and soil respiration rates are likely to be reduced (Aber and Magill, 2004).

In the long-term, the micro-organisms responsible for N_2O and NO production, the nitrifiers and denitrifiers, will successfully compete for the deposited N, and correlations between N deposition rate and N_2O emissions have been demonstrated for forests and moorlands (Pilkington *et al.*, 2007; Skiba *et al.*, 2004). Atmospheric N deposition-induced emissions of N_2O are included in the Intergovernmental Panel on Climate Change (IPCC) methodology (indirect emissions); it is assumed that 1% of the N deposited is emitted as N_2O (IPCC, 2006).

Forest ecosystems tend to be net sinks for CH_4, whereas moorlands are often net sources of CH_4. In the latter, some of the CH_4 produced in the anaerobic soil layers is oxidised in the surface layers, thereby reducing the net emission rate. The general view has been that CH_4 oxidation is inhibited by N addition, leading to increased emission rates in moorlands and reduced oxidation rates in forests (e.g. (Butterbach-Bahl *et al.*, 2002; MacDonald *et al.*, 1997; Sheppard *et al.*, 2009). Recent publications, however have shown that N additions can also stimulate CH_4 oxidation rates (Bodelier and Laanbroek, 2004).

The source of atmospheric N deposition (wet, dry, reduced, oxidised) does not appear to influence N_2O and NO emission rates, but does have an impact on soil CH_4 fluxes. The N component of atmospheric deposition may inhibit or stimulate CH_4 emissions, whereas the sulphur component of acid rain inhibits CH_4 emissions in moorlands (Gauci *et al.*, 2005). Recent evidence suggests that the flux of methane CH_4 from wetlands could also be altered by ozone, although the direction of the effects is not consistent (Mörsky *et al.*, 2008; Toet *et al.*, 2011).

In terms of vegetation, N is often a limiting factor for tree growth. Several studies have used large forest inventory datasets, along with climate and other environmental data, to determine the causes of observed growth changes in forests (Nellemann and Thomsen, 2001; Solberg *et al.*, 2004); these studies have suggested that in Europe the majority of changes in forest growth increment can be accounted for by N deposition and very little by elevated CO_2 and climate change. A recent study has confirmed that increased tree growth rate (5-20% increase in net primary production (NPP) over the period 1920-2000) is widespread across Europe (Kahle *et al.*, 2008) and attributed ~66% of these increases to the effect of nitrogen deposition using four different models (van Oijen *et al.*, 2008).

A recent analysis of the net C budgets for European forests has shown a strong correlation between rates of N deposition and C sequestration (Magnani *et al.*, 2007). However, the impact of N deposition on tree growth is not precisely quantified, with estimates of dC:dN (the increased ecosystem sequestration of carbon per unit of added N) ranging from 0-10 to over 200 kg C kg^{-1} N. Magnani *et al.* (2007) found that rotation-averaged net ecosystem production (NEP) displayed a strong correlation with N deposition in around 20 northern temperate forest sites, suggesting a mean dC:dN of around 200 kg C kg^{-1} N (N deposition adjusted as total deposition). However, the variation in NEP may partly be explained by other potential driving variables such as temperature (de Schrijver *et al.*, 2008; de Vries *et al.*, 2008; Högberg, 2007; Reay, 2007; Sutton *et al.*, 2008). Combining modelling and empirical data from plots across Europe, de Vries *et al.* (2006) suggested a dC:dN of around 46 kg C kg^{-1} N (21 kg C kg^{-1} N in trees).

It is, nevertheless, important to emphasise that any positive effect of N deposition on C sequestration may occur alongside adverse effects on sensitive ground flora or epiphytic lichens, and that in areas with continued high rates of N deposition, there may be adverse effects on tree vitality and growth, associated with nitrogen saturation and leaching.

In contrast to N deposition, experimental studies show that O_3 significantly reduces carbon sequestration in plants and soils. A recent global modelling study suggests that O_3 feedback effects on vegetation could significantly amplify the radiative forcing due to increases in tropospheric ozone; Sitch *et al.* (2007) predicted a reduction due to O_3 in land C uptake of 143 PgC, which is equivalent to a reduction of 17% in the projected land C uptake in response to increasing CO_2 concentrations over the century. Such a suppression of the land C sink results in additional anthropogenic CO_2 emissions accumulating in the atmosphere, and therefore an indirect radiative forcing of climate by O_3.

5.6 Implications for policy

The previous sections, covering soils, waters and vegetation, show that acidification, N deposition and O_3 are significant threats to sensitive semi-natural habitats in the UK and will remain so in 2020 despite significant falls in emissions and substantial recovery from the effects of acidification. It is estimated that in 2020, 39% of sensitive habitats in the UK will still exceed the critical load for acidity, with 48% still exceeding the critical load for nutrient nitrogen (Hall *et al.*, 2006a). This is a major concern in relation to the protection of biodiversity and has implications for meeting national and international conservation policy targets and obligations. This concern is demonstrated by the incorporation of critical loads exceedance in UK biodiversity indicators which help measure progress towards the target to halt the loss of biodiversity by 2010. The Habitats Directive requires Member States to take measures to maintain or restore natural habitats at a favourable conservation status. Under Article 17 of the Directive, Member States must report every six years on the implementation of the Directive. The UK submission in 2007 included an assessment of acid deposition and nutrient nitrogen deposition impacts on sensitive habitats covered by the Directive (JNCC, 2007). The assessment was based on application of critical load exceedances and showed acid deposition and N deposition are a “current pressure to structure and function” and a “threat to future prospects” of a substantial proportion of sensitive habitats in the UK. Ozone was excluded from the exercise because of a lack of an appropriate assessment method, but was highlighted as an important regional pollutant.

The Habitats Directive establishes a network of protected sites, Special Areas of Conservation, to ensure the long-term protection of valuable or threatened habitats and species. Domestic biodiversity policy and legislation is also strongly based around protected sites, i.e. Sites of Special Scientific Interest (SSSIs) in England, Scotland and Wales or Areas of Special Scientific Interest (ASSIs) in Northern Ireland. The Joint Nature Conservation Committee (JNCC) has developed common standards for site monitoring of those special features for which the site was designated which are assessed to determine whether or not they are in favourable condition, and to identify the possible causes of unfavourable condition (Williams, 2006). The problems of interpreting the results of surveys and experiments in terms of the long-term ecological impacts of both N deposition and O_3, rather than management, climate or other factors, were highlighted in previous sections. It is even more difficult to directly detect or attribute the impacts of these pollutants on individual sites and thus current reporting on the condition of A/SSSIs is likely to substantially under report the impacts of air pollution (Hall *et al.*, 2006b). This is a major concern since these assessments are a key policy driver (i.e. for addressing the causes of unfavourable condition) and are also crucial to informing the conservation status assessment for Article 17 reporting. Therefore, there remains a significant gulf between results of risk assessment approaches, such as critical loads, and of national surveys, and evidence from individual protected sites. This is partly due to the way monitoring is currently undertaken on sites, but also because of the extreme complexity of the interactions between air pollution impacts, management and other abiotic and biotic influences. These practical challenges have substantial implications for evidence-led policy. However, there are a number of initiatives underway to try and address these issues in time for the next reporting round.

5.7 Natural capital and ecosystem services

A useful concept which can help illustrate the implications of reported changes is that of change in ‘natural capital’, its function and thus ‘ecosystem services’. The latter are defined as:

> “The services that the environment provides that people need.”

This approach was developed in the Millenium Ecosystem Assessment (2005). Subsequently, it has been used by Defra to develop an ‘ecosystems approach’ for application in policy development and regulation; the ecosystems approach has been designed to include a holistic assessment considering the full range of ecosystem services, and hence to provide insights into the full costs and benefits of policy measures (Haines-Young and Potschin, 2007). Air pollution may enhance or reduce the stock of natural capital, its function and therefore the delivery of ecosystem services. The potential for an ecosystem approach to be applied to policy on control of emissions of air pollution was demonstrated by Hicks *et al.* (2008) who showed that different options for regulation of agricultural ammonia emissions would have different effects on a range of ecosystem services. However, a more comprehensive assessment of the impacts of air pollution on natural capital, ecosystem function and services has not yet been developed for the UK. One of the major challenges is to identify biophysical measurements which can be monitored to quantify both stock and change of ecosystem services. Table 5.14 provides a summary of the potential impacts of air pollution on a range of biophysical measurements which can be linked to ecosystem function and service. Evidence of a potential impact whether positive or negative is indicated together with the evidence base drawn from the RoTAP effects chapter (Table 5.5).

Table 5.14: Potential impact of air pollution on ecosystem services and biophysical measurements which provide an indicator of change in ecosystem function.

Ecosystem service	Potential impact (+ or –) of air pollution	Biophysical measurement available as an indicator of change reviewed in RoTAP	RoTAP section where evidence is reported
Food, Fuel, Fibre	(+) S and N deposition increase nutrient availability for crops	N and S content of crops and trees	Section 8.8.3
	(-) High Al and H^+ in surface waters have toxic effects on salmonid populations and other acid-sensitive species that sustain fish	Change in fish densities, and macroinvertebrate and algal populations in monitored rivers and lakes	Section 5.3.2
	(-) O_3 decreases production of sensitive crops and trees and reduces forage quality in grasslands	Crop yields and economic production Forest growth rates	Section 5.4.8
	(+) Regional N deposition enhances forest production	Forest growth rates	Section 5.5.4
Air Quality Regulation	(+/-) Changes in growth, species composition and surface characteristics can alter rates of pollutant deposition	Changes in growth and species composition Changes in deposition velocity	Chapter 3 and Section 5.4
Water Flow and Quality	(+) S and N can enhance primary production increasing soil carbon stocks and slowing decomposition and thus increase water storage and filtration	Soil organic matter content	Sections 5.2.1 and 5.5.4
	(-) Transfer of pollutants through soils into water	Soil solution chemistry	Sections 5.2.1 and 5.2.2
	(-) Acidification of freshwater	Stream and water chemistry and biota change	Section 5.3.2
	(+/-) O_3 can increase or decrease transpirational losses, altering water retention in summer	Leaf stomatal conductance or plant canopy transpiration	Section 5.5.3
Climate Regulation	(+) N-induced increased primary production and above ground C sequestration	Increased forest growth	Section 5.5.4
	(+) Increased soil carbon storage through N and S enhanced primary production and/or slower decomposition rates	Increased soil organic matter content	Sections 5.2.1 and 5.5.4
	(-) N-induced increased N_2O emissions	N_2O fluxes from long-term experiments and across deposition gradients	Section 5.5.4
	(-) O_3 reduces above and below ground growth and carbon storage	Above-ground and below-ground biomass and production	Sections 5.4.8 and 5.5.4
	(+/-) O_3 may influence soil methane fluxes in wetlands	Methane fluxes	Section 5.5.4

Ecosystem service	Potential impact (+ or –) of air pollution	Biophysical measurement available as an indicator of change reviewed in RoTAP	RoTAP section where evidence is reported
Genetic Resources	(-) Increased N availability in semi-natural systems causes change in plant species composition or decrease in plant species richness	Plant species richness Plant species composition Acidity and fertility indices	Sections 5.2.1 and 5.4.2
	(-) Acidic deposition will cause plant species change	Plant species composition Acidity indices	Section 5.4.2
	(-) Acidification results in a reduction in aquatic diversity at several trophic levels	Aquatic macrophytes, macroinvertebrates and fish	Section 5.3.4
	(-) N deposition and acidification results in reduction in soil biodiversity	Soil mesofauna composition and indicator organisms Soil bacteria composition	Section 5.2.1
Pollination	(-) N deposition causes reduced species richness and reduced flowering of forb species in grasslands	Decrease in frequency and flowering of forb species	Section 5.4.2
	(+) N deposition increases flowering in heathlands	Increase in flowering of heather	Section 5.4.2
	(-) O_3 decreases flowering in woodland bulb species	Woodland flower production	Section 5.4.8
Aesthetic	(-) N enrichment and O_3 can cause decline of characteristic and attractive species	Change in plant species composition	Sections 5.4.2 and 5.4.8
	(+) Acidification results in the clarifying of peat-stained waters	Change in dissolved organic carbon concentrations	Section 5.3.2

No review of the implications of air pollution impacts on other services associated with social and cultural services has been carried out for this report. While effects such as loss of characteristic plant species or loss of fish populations have implications for such services they are location- and population-specific and are beyond the scope of this review.

Chapter 6 Heavy Metals

Summary

- The UK National Atmospheric Emissions Inventory provides spatially disaggregated emissions of arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), selenium (Se), tin (Sn), vanadium (V) and zinc (Zn).
- Emissions of heavy metals have significantly decreased since 1970. For most metals, this has been caused by reduced consumption of coal and the decline of heavy industry in the UK. For many metals, industrial processes in the ferrous and non-ferrous metals industry are now some of the most significant sources of emission. UK emissions of Pb, Cd and Hg have significantly decreased since 1990 in compliance with the 1998 UNECE Protocol on Heavy Metals. Additional legislation exists at national and local scales to control emissions from industrial activities including municipal solid waste (MSW) Incinerators.
- Concentrations of heavy metals in air have declined since the 1970s. Concentrations of Ni, Zn and Cd in soils have declined, but Cu, Pb and Hg concentrations are unlikely to decline for centuries. Concentrations of Pb, Hg and probably Cu in some habitats, such as freshwater lochs, may still be increasing.
- UK maps of concentration and deposition of heavy metals in air, rainfall and moss samples are available. Concentrations of heavy metals in the atmosphere are generally largest in the south and east of the UK, although deposition, which is strongly influenced by rainfall, is highest in upland areas in the north and west of the country.
- Emission estimates of heavy metals for the UK do not agree with measured concentrations and deposition budgets. The measurements available indicate larger emissions of metals than those provided by the NAEI by factors ranging from 2 to 10. The emissions of Pb, Zn and Cu are among those for which the inventory is least satisfactory. Although some of the factors responsible for this discrepancy have been identified, including under-representation of fugitive emissions from industrial activities in the inventory, and the inclusion of resuspended material and natural sources in the measurement data, there is currently too little quantitative information to identify the sources of much of the metals present in air over the UK.
- Critical loads based on ecosystem effects have been calculated for Cd, Pb, Cu, Ni and Zn for six UK habitats. Exceedances of critical loads for non-forest and managed coniferous woodland are low for all metals, although over 50% of areas of managed broadleaved woodland and unmanaged woodland exceed the critical loads for Cu, Pb and Zn.
- Critical limits for the effects of heavy metals on biota reflect current concentrations in soil, which may arise from current or past deposition, or underlying geology. Where these limits are exceeded there is a risk to biota; for Cu over 50% of broad-leaved woodland is at risk, and for Zn over 25% of all six UK habitats is at risk.
- In many soils there is a large legacy of historic deposition which is currently not available to biota because it is strongly bound to soil organic matter. Any decrease in soil organic matter, for example in response to climate change, would risk releasing this store of metal into the environment in a bioavailable form.

6.1 Heavy metal emission estimates

Air emissions of heavy metals[12] arise from a wide range of different sources. Trace quantities are found in fossil fuels, and several industrial processes give rise to emissions of specific metals. The relative contributions of these sources to the emissions total vary by metal, resulting in a unique source profile for each metal. For example, emissions of vanadium (V) are almost exclusively from oil combustion, lead (Pb) emissions used to be almost completely from road transport but are now dominated by activities in the iron and steel sector, and the largest source of arsenic (As) is the disposal of treated wood by burning. This is shown in Figure 6.1 below.

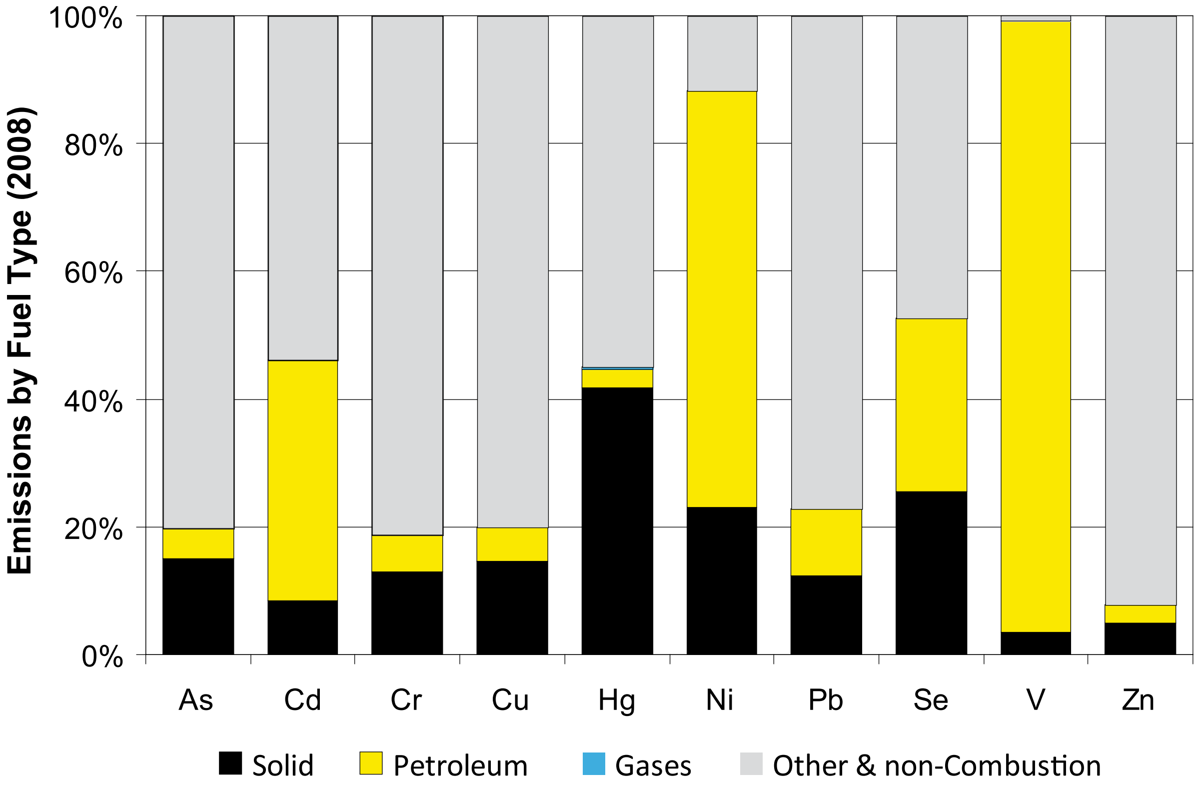

Figure 6.1: Metal emissions by source type (Murrells *et al.,* 2010).

Space does not permit a detailed assessment of the emissions of all heavy metals in this chapter; examples of some of the more important metals (in terms of legislation and human health) are presented – details for other metals are given on the National Atmospheric Emissions Inventory (NAEI) website (http://www.naei.org.uk/).

For combustion sources, the most common methodology for estimating emissions has been to combine the metal content of the fuel with the amount of fuel consumed at

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[12] The term 'heavy metal' is used here to denote a metal which is of importance due to its potential impacts on health. It is not used in line with the precise definition given in inorganic chemistry, but includes elements such as arsenic and selenium.

the national scale. There is little information on metal content, which is likely to vary greatly over time. However, more point source data have become available from the larger industrial plant, and this has allowed considerable improvements to the emission estimates. Emissions from a few industrial sites can include a very significant fugitive component (i.e. not emitted through a controlled exhaust system). These emissions are considerably more difficult to estimate and there is a general lack of literature on the rates of fugitive emission. Non-industrial fugitive sources include brake and tyre wear, and the burning of treated wood. This chapter focuses on emissions and deposition of heavy metals within the UK; a significant fraction is exported and imported, but the transboundary components are even more uncertain than UK emissions (Section 6.7).

Historic emission estimates for 13 different heavy metals are available from the UK National Atmospheric Emissions Inventory[13] (NAEI). These are: arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), selenium (Se), tin (Sn), vanadium (V) and zinc (Zn). There are currently no emission projections for the UK. The following sections briefly consider Pb and Hg. Details on emissions of all metals can be found in Murrells *et al.* (2010).

6.1.1 UNECE Heavy Metals Protocol

The 1998 UNECE Protocol on Heavy Metals (www.unece.org/env/lrtap/), to which the UK is a signatory, targets the emissions of three metals: Pb, Cd and Hg. This commits the UK to reducing emissions of these metals to below emission levels in 1990. The Protocol also specifies limit values for emissions from stationary sources and requires 'Best Available Technology' to be used in reducing emissions from these sources. Examples include the use of filters or scrubbers for combustion sources and mercury-free feedstocks for production processes. The Protocol also required countries to phase out leaded petrol. Under the Protocol, measures have been introduced to reduce heavy metal emissions from other products, e.g. Hg in batteries, and examples are given of management measures for other Hg-containing products.

6.1.2 Emissions of lead (Pb)

Figure 6.2a shows UK emissions of Pb. The observed decreases in Pb emissions are primarily the result of changes in the Pb content of petrol. In the late 1990s unleaded petrol[14] was introduced, and there was a gradual decrease in the use of leaded petrol, until 2000 when it was completely withdrawn from general sale (being replaced by lead replacement petrol).

The huge reduction in emission from the use of petrol now means that although emissions from other sources have reduced as well, these now contribute a significant fraction of the emissions total. Between 1985 and 2008, the contribution from road transport fell from 89% to 2%, the contribution from the industrial sector (including electricity generation) correspondingly increased from 10% to 87%. Emissions from iron and steel production are now the largest sources of Pb.

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[13] http://www.naei.org.uk

[14] The name 'unleaded petrol' is in fact misleading. Whilst no lead is added to the fuel, it is still present as a trace element, but at concentrations less than 1/1000th of those in 'leaded' petrol.

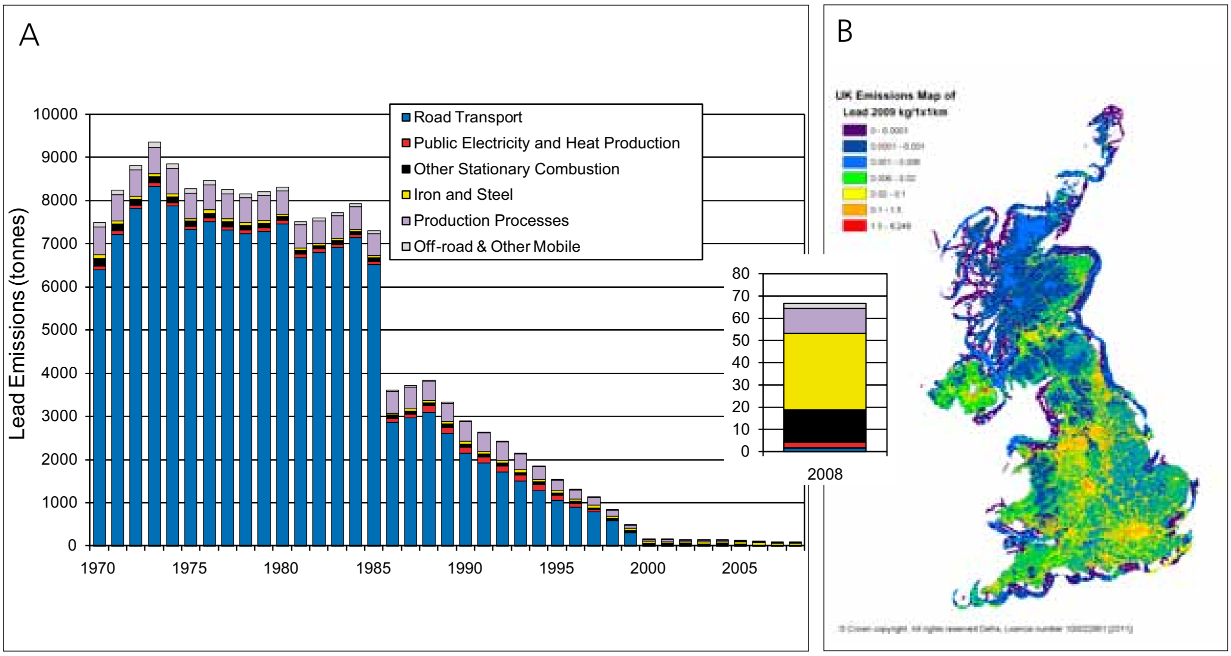


Figure 6.2: (a) UK emissions of Pb (Murrells *et al.*, 2010); (b) Mapped Pb emissions for 2009 (NAEI, 2010).

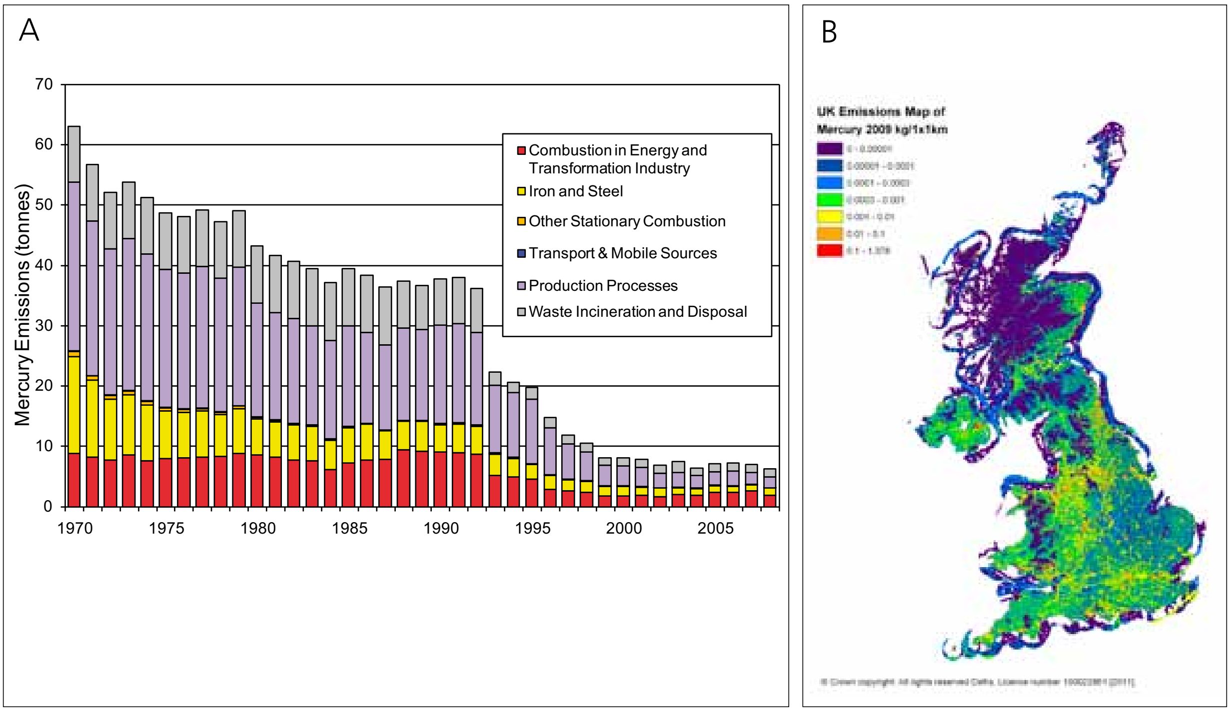
The UK emissions map of Pb is shown in Figure 6.2b. In line with the greatly reduced emission from road transport, the spatial distribution of Pb in the UK has changed significantly. Emissions are now dominated by a small number of industrial point sources. This change also means that the majority of emissions are now from high level sources, resulting in more effective dispersion.

A Monte-Carlo uncertainty analysis of Pb emissions gives a 95% confidence interval of -20% to +30%. Uncertainties and validation studies are considered in more detail in Section 6.1.4.

6.1.3 Emissions of mercury (Hg)

Figure 6.3a shows UK emissions of Hg. In the early part of the time series, emissions fall steadily as the iron and steel industry in the UK declines. There is a significant step change between 1992 and 1993; this is associated with legislation introduced to control emissions from MSW (municipal solid waste) incineration and crematoria. In addition this is a period of more extensive gas use, at the expense of coal (a source of Hg), in electricity generation. Hg emissions arise from a number of production processes, but the most important is the manufacture of chlorine from Hg cells. Improved controls and the introduction of membrane cells have given rise to emission reductions in the more recent portion of the time series shown in Figure 6.3a.

Figure 6.3b shows the Hg emissions map. The majority of emissions are from point sources, and it is evident that industrial areas give relatively high emissions, corresponding to the source apportionment explained above. There is only a weak correlation with urban centres.



Figures 6.3: (a) UK emissions of Hg (Murrells *et al.*, 2010); (b) Mapped Hg emissions for 2009 (NAEI, 2010).

Hg is emitted into the air in several different forms: as gaseous elemental Hg (relatively unreactive), as a component of particulate material, and as reactive gaseous Hg (usually in oxidised form). These three forms are estimated to contribute approximately 55%, 5% and 35% respectively to total emissions (Dore *et al.*, 2008).

A Monte-Carlo uncertainty analysis of Hg emissions gives a 95% confidence interval of -30% to +40%. Uncertainties and validation studies are considered in more detail in Section 6.1.4.

6.1.4 Uncertainties in metal emission estimates

Modelling studies and measurements suggest that emission estimates for a number of metals in many European countries are significantly underestimated (see Section 6.3). UK estimates of metal emissions are considered to use the current best science and follow best practice for inventory compilation. So the question is, why does there appear to be a significant shortfall in emission estimates? There are a number of possible explanations.

Uncertainties, systematic errors and bias

As part of the inventory compilation, a Monte-Carlo analysis has been conducted on the emission estimates. However, whilst this provides a reflection of the uncertainties associated with the data included in the calculation methodology, it cannot account for the impact of missing or unknown sources. In addition, it may be that the uncertainty profiles assigned to individual sources systematically underestimate the levels of uncertainty. For example, an industrial plant operator may monitor stack emissions on a frequent basis, and report emission estimates to a high degree of accuracy to the regulator (e.g. the Environment Agency). However, it may be that there are significant fugitive emissions from plant activities, which are not captured at all by stack monitoring. This may result in a significant underestimate of emissions, even though the data are accompanied by an uncertainty range that might suggest that the emissions are well-characterised. However, in the UK there are now only a few large industrial sources. Furthermore, there are some sources in the inventory, such as the burning of treated wood, where overestimation is more likely.

Variability in emission factors

There have been several studies conducted recently which have investigated the accuracy of estimates of metal emissions (Dore *et al.*, 2008; ESPREME, 2007; van der Gon and Appelman, 2009; van der Gon *et al.*, 2005; van der Gon *et al.*, 2007). Here we consider Pb emissions from road transport by way of example. A range of emission factors is currently used by different European countries for estimating metal emissions. In the road transport sector, some countries assume that the use of unleaded petrol gives no emissions of Pb, whilst others use an emission factor derived from the limit value of Pb in petrol (5 mg l^{-1}). In the NAEI, a value of 0.04 mg l^{-1} is used (UKPIA, 2003), which is derived from extensive measurements, and 70% is assumed to be released to air. Van der Gon (2009) concludes that Pb from road transport is not underestimated in the UK emissions inventory. This highlights the wide range of assumed emission factors, for a source which is generally considered to be well-characterised, and where it is possible to use a straightforward estimation methodology.

Another example of uncertainty is the metal content of fuels and the fraction of metal retained in ash, both of which vary depending on the exact origin of the fuel. The coal that is currently consumed in the UK is primarily imported from Russia and South Africa. Several decades ago it would have been sourced from Wales. The metal content of coal from different locations, even within the same region, is known to vary greatly, potentially by several orders of magnitude. In the NAEI, large point sources will report emissions of metals from stack measurements, but emissions from smaller point sources and area sources will be calculated using a metal content of the fuel. The most current value for the metal content of the fuel is used and is not varied across the time series because of a lack of historical data, but this practice may disguise very large variations.

Primary emissions and resuspension

It is important to recognise that the UK NAEI is a ‘primary’ emissions inventory. It does not typically include emissions from resuspension. Significant levels of all metals are expected to have been emitted since the start of the industrial revolution, and deposited to the land and sea. As a result, it is possible that the resuspension of surface material could give rise to a significant source term. Currently, the relative importance of this resuspension component at the national scale is not well known, although there are modelling studies which have attempted to include a resuspension component (see Section 6.7).

Missing sources and underestimation

Emissions of metals from natural sources are not included in the NAEI. Initial indications are that these are not large. It is thought that the most likely source of underestimation in the emissions inventory arises from fugitive industrial emissions. However, more work is needed before the magnitude of this term can be quantified.

There are several other sources which may provide emissions not yet included in the NAEI:

- Accidental/malicious fires (dwellings, factories, other buildings, vehicle fire, etc.)
- Demolition
- Corrosion/abrasion of metal structures
- Galvanizing
- Non-thermal processing of scrap metals (e.g. shredding of scrap metal)
- Part B industrial processes (e.g. cement batching, quarrying, powder coating, etc.)
- Abrasion of road surfaces by motor vehicles.

6.1.5 Impacts of climate change on emissions of metals

Nearly all metal emissions arise from either fuel combustion or specific production processes. As a result, the main factors impacting on future emissions are:

- The amount, and mix, of fossil fuels consumed;
- The activity levels of relevant production processes; and
- The levels of emissions abatement applied to these activities.

The direct impact of climate change on these emissions will be limited. However, Government policy to reduce greenhouse gas emissions will drive future levels of fossil fuel combustion. At the moment there is no clear future energy strategy, and so several different outcomes are possible. Most of the options are likely to lead to reduced emissions of metals. If 'clean' coal (with carbon capture and storage technology) is promoted, then this will give rise to increased fuel consumption and increased metal emissions. However, it is likely that the emissions of particulate matter (PM) would be raised as a health concern, and ensuring the control of PM emissions would have an impact on the emissions of metals.

Increased temperatures could give rise to elevated natural emissions, but it is not possible to comment with any certainty on whether these increases would have a significant impact on total emissions to air. Perhaps more importantly (see Section 6.8 below), the remobilisation of the large stock of heavy metals in UK soils could be accelerated if changes in climate lead to more rapid breakdown of organic matter in soils, with implications for increased metal concentrations in soil solution and freshwaters, and increased exposure of biota.

6.2 Concentration and deposition data from the UK Rural Heavy Metals Monitoring Network

Measurements of heavy metal concentrations in UK air go back over 50 years (Section 6.9). The Department for Environment, Food and Rural Affairs (Defra) currently funds two networks which measure the atmospheric concentration of heavy metals in the UK. The rural network is managed by the Centre for Ecology and Hydrology (CEH) (Malcolm *et al.*, 2010) and the urban network is managed by the National Physical Laboratory (NPL) (Brown *et al.*, 2009).

The Rural Heavy Metals Network has been managed by CEH since 2004. The network comprises 15 sites in rural locations which are unlikely to receive significant emissions from local point sources. In addition to measuring concentrations of the metals in air and in precipitation, dry and wet deposition values are calculated. The data are used to produce annual maps of heavy metal concentrations and deposition for rural UK. Additional monitoring takes place to measure heavy metal concentrations in cloud water collected from two upland sites, and speciated Hg (elemental, 'reactive gaseous' and particulate) at one site, Auchencorth Moss, in southern Scotland. Details of the concentrations and deposition of each metal can be found at http://www.uk-pollutantdeposition.ceh.ac.uk for each of the years since rural sampling started. Examples of maps for air concentration, rain concentration and total deposition of copper are shown in Figure 6.4; maps for the other metals are available from the website. Many metals show a similar spatial pattern, with highest air concentrations in the south and east, and lowest concentrations in the north and west. Patterns in precipitation are more variable between metals, with higher concentrations in the midlands of England. However, deposition of all metals is dominated by wet deposition, which in turn depends more on the variation in the amount of precipitation across the UK than on the variation in concentration, so that the highest deposition is seen over the mountains of the west and north. The overall deposition budgets for 2007 are presented in Table 6.1, showing the predominance of wet deposition, and the small contribution over the whole country of direct cloud deposition (<2%). However, the contribution of cloud deposition is locally important in mountainous areas of the north and west. The overall deposition of each metal, based on rural measurements, is considerably greater than the current estimates of emissions from the UK, as discussed later.

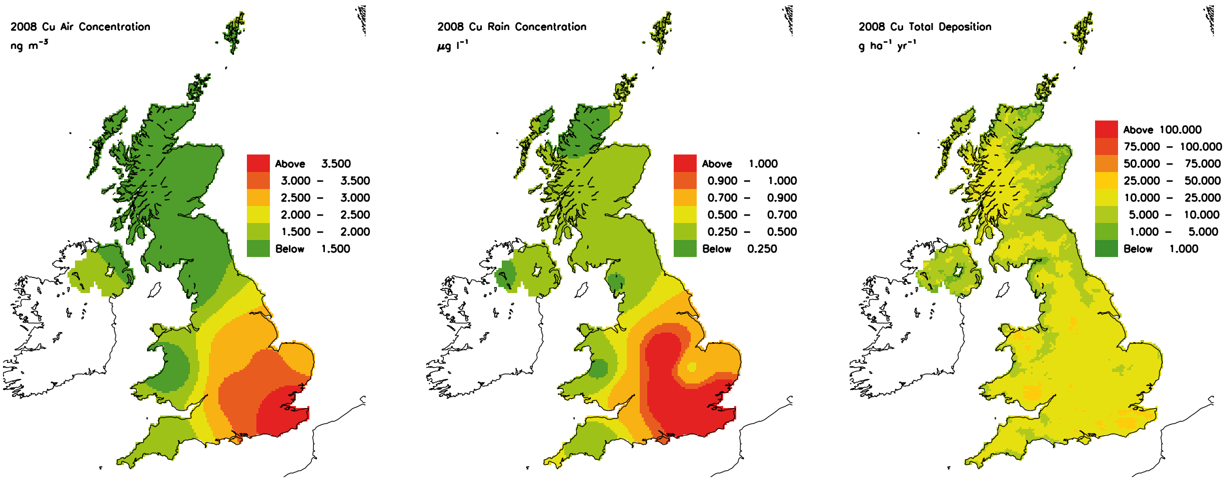


Figure 6.4: Concentrations and deposition of copper (Cu) across the UK in 2008, from left to right: Cu concentration in air (ng m^{-3}), in rain (ng l^{-1}) and total deposition (g ha^{-1} yr^{-1}) (Malcolm et al., 2010).

Table 6.1: Summary of UK heavy metal deposition estimates (tonnes yr^{-1}) as components of wet, dry and cloud deposition for 2008 (Amount in parenthesis is percentage of total deposition (Malcolm *et al.*, 2010).

t yr^{-1}	As	Cd	Cr	Cu	Ni	Pb	Se	V	Zn	Hg
Total UK deposition	71	9.3	66	327	92	309	85	165	1810	2.1
Dry deposition	19 (27%)	2.4 (26%)	35 (53%)	104 (32%)	27 (29%)	97 (31%)	15 (18%)	57 (34%)	350 (19%)	Not known
Wet deposition	51 (72%)	6.8 (73%)	30 (46%)	217 (67%)	64 (70%)	208 (67%)	67 (80%)	106 (64%)	1440 (80%)	2.1
Cloud deposition	0.9 (1.2%)	0.2 (1.7%)	0.8 (1.2%)	5.7 (1.7%)	1.4 (1.5%)	4.4 (1.4%)	1.9 (2.2%)	2.4 (1.5%)	20 (1.1%)	0.04

In addition to the UK rural network there is another long-running network of measurements of heavy metals in air (but not precipitation) at urban and industrial sites, which was extended from 17 to 24 sites in 2007 to meet the requirements of the 4th Daughter Directive of the European Air Quality Framework Directive 96/62/EC (Brown *et al.*, 2008). One of the 'urban and industrial' sites (Eskdalemuir) is classified as 'rural', and so provides an independent check on values obtained by the rural network. From a comparison of 2004-07 data (Figure 6.5), the average concentration of all metals in air is generally within 30% of the average of the concentrations measured at Auchencorth and Cockley Beck (approximately equidistant, ~100 km to the north and south of Eskdalemuir). The exceptions are copper and chromium, which are significantly higher and more variable from year-to-year at Eskdalemuir. However, the good agreement for this period suggests that there is no large-scale methodological bias between the networks. The two 'urban background' sites at London (Horseferry Road) and Motherwell show generally larger concentrations than the average for the rural network, as expected for urban sites. The lowest enhancements are for vanadium, arsenic, cadmium and lead (all 1.4-2 times the rural mean), and the greatest enhancements are for iron and copper (more than 4 times the rural mean), particularly in London. Average concentrations from 'industrial' sites are much greater, at up to 10 times the rural network average for copper.

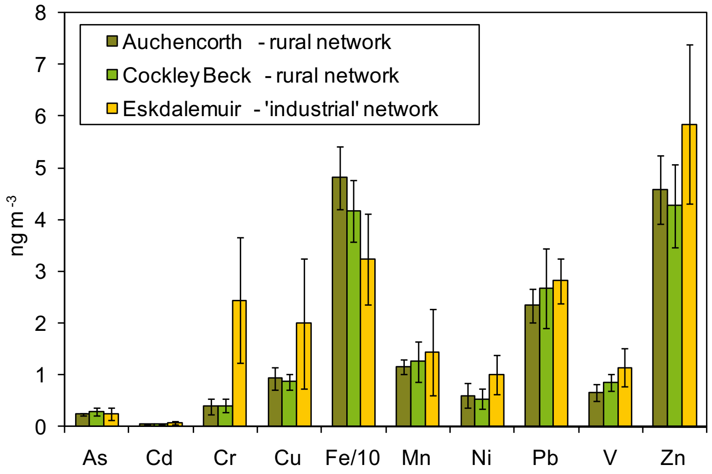


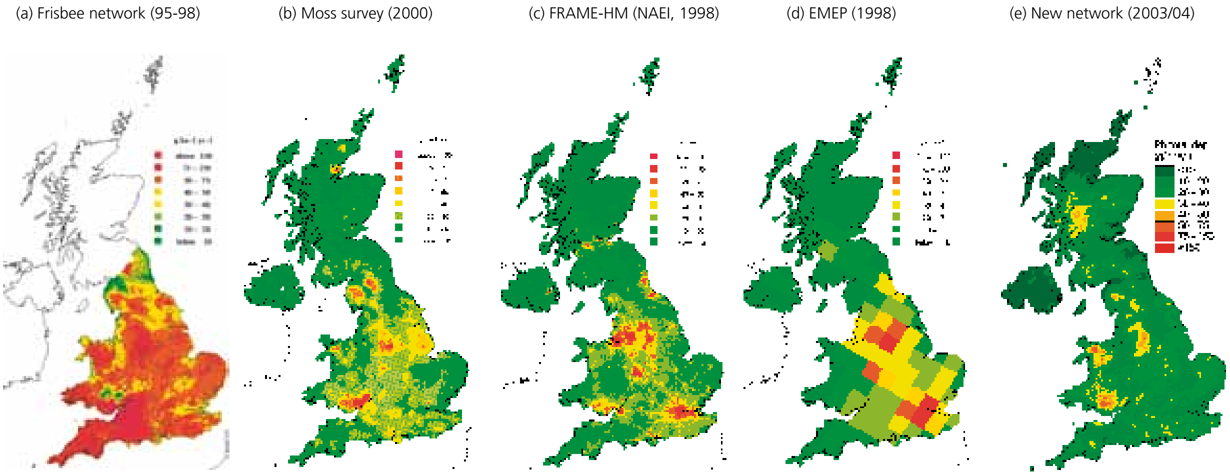
Figure 6.5: Comparison of rural site air concentrations from both UK heavy metal monitoring networks 2004-2007 (see text) (Error bars denote standard deviation across years). Source: RoTAP.

6.3 Comparison of deposition and emissions

Several methods are available to monitor metal concentrations in air and deposition, in addition to the samplers currently used in the UK networks. Active sampling of atmospheric particles has provided air concentration data at rural sites for over 50 years (Figure 6.14, Section 6.9). Different types of deposition sampler have different efficiencies for trapping particles; one type of bulk sampler, using an upturned saucer ('Frisbee'), collected wet and dry deposition and recorded much higher concentrations than a standard precipitation collector (Alloway *et al.*, 1998; Fowler *et al.*, 2006). However, it has not been possible to relate deposition sampled by this type of collector to deposition to vegetation or other surfaces. Instead, dry deposition is calculated on the basis of the measured air concentration of particles, and the appropriate deposition velocities based on surface roughness and particle size, where such measurements exist. Estimates of deposition (wet and dry) to vegetation such as moss have been inferred from the accumulation of heavy metals in plants, as described below. A comparison of several methods for assessing deposition is shown for lead, which is known to accumulate in plant tissue, in Figure 6.6. Methods of generating the modelled deposition (Figures 6.6c and 6.6d) based on official emission statistics are described below, but it can be seen that different methods lead to different values across the country, with the smallest overall deposition obtained from the rural network (Figure 6.6e). Nevertheless, the overall deposition for the UK shown in Table 6.1 is still many times greater than the estimated emissions for 2005, as shown in Table 6.2. In all cases, except vanadium (V) and mercury (Hg), more metal is deposited than is estimated to be emitted from the UK. Independent estimates of material imported into the UK suggest that imports cannot explain the difference, implying that one or more important sources of metal emissions have not been included in the emissions estimates. The size of the discrepancy is much greater than the combined uncertainty in the measurements and interpolated deposition: the uncertainty in chemical analysis is generally ±10%; there may be a positive bias of up to 30% caused by dry deposition on the precipitation samplers; our knowledge of the appropriate deposition velocities for dry deposition may be uncertain by a factor of 2 (but this contributes only a minor proportion of total deposition); and there may be uncertainties of around ±20% in the mapping process. Collectively, however, these do not generate a factor of 5 (or greater) difference between the emissions inventory and the measurements, as shown in Table 6.2 for Pb, Zn, Cu and As. In fact deposition of metals to the UK landscape is only expected to capture a small fraction (between 20 and 40% of emissions) as the majority of small particles would be expected to advected out of the country by wind.

Table 6.2: Metal emissions and deposition over the UK in 2005, based on the rural monitoring network ('measurements') and modelled (FRAME) based on the emissions (NAEI). Source RoTAP.

tonnes yr^{-1}	As	Cd	Cr	Cu	Ni	Pb	Se	V	Zn	Hg
Emissions NAEI	14	4	36	60	87	118	49	960	461	7.6
Import	3	2	18	32	18	35	19	n/a	344	n/a
Deposition FRAME (based on NAEI)	7	4	22	57	59	86	30	n/a	490	n/a
Measured deposition	73	10	52	333	155	398	85	203	2190	1.8
Measured deposition/ Modelled deposition	10	2.5	2.4	5.8	2.6	4.6	2.8	n/a	4.5	n/a



(a) Frisbee network (95-98)

(b) Moss survey (2000)

(c) FRAME-HM (NAEI, 1998)

(d) EMEP (1998)

(e) New network (2003/04)

Figure 6.6: Deposition of lead (Pb) across the UK using different methods (a) Interpolated wet+dry deposition using 'Frisbee' collectors; (b) Based on calibrated measurements in moss (see Section 6.4.2); (c) Modelled using FRAME and NAEI emissions (see Section 6.7); (d) Modelled using EMEP and European emissions (see Section 6.7); (e) Interpolated from rural network measurements (earliest year available) (Note that emissions of lead decreased by a factor of 10 between 1995 and 2000, but there was little change between 2000 and 2004 (see Figure 6.2a).) (Fowler *et al.*, 2006).

This conclusion is not confined to the UK, but the UK is the first country to establish a network of rural stations to quantify dry and wet deposition of metals for direct comparison with emission estimates. The European Monitoring and Evaluation Programme (EMEP) concluded that the emissions inventories are deficient for most metals across Europe (Ilyin *et al.*, 2008). Systematic errors are widespread and there are no validation studies. An independent assessment of emissions conducted by the ESPREME project concluded that a similar underestimate of metal emissions was made in European countries' official statistics (ESPREME, 2007).

Some of the 'missing' emissions may arise from industrial processes that are not monitored, and some may be caused by resuspension (by wind or mechanical action, e.g. traffic) of material from the surface, but attempts to estimate emissions from such sources have not yet been able to address the imbalance for the UK. Estimates from elsewhere in Europe suggest that wind-driven resuspension can account for greater emissions than reported primary sources (Iyin *et al.*, 2008). One recent UK study (Abbott, (2008) has used dispersion modelling to compare concentrations produced by resuspension from agricultural activities and roads, incorporating meteorological conditions, surface soil metal concentrations and land use data for each 1 km^2 of the UK. Although the modelled concentrations from resuspension were well correlated across the UK with the measured rural air concentrations, they could only account for a few percent of the measurements – insufficient to explain the discrepancy between emission estimates and measurements, although they did amount to between 15% and 35% of the official emissions estimates. The use of an integrated soil core concentration from the top 15 cm, rather than surface soil concentrations, is likely to have led to an underestimate of the true resuspension. This work is being pursued further. Resuspension as droplets (e.g. from wet roads) was also not considered. The contribution of non-exhaust particle sources from road traffic has been reviewed recently, and it was concluded that although some metals may be useful tracers of brake or tyre wear, source identification is confounded by the complexity of the processes involved (Thorpe and Harrison, 2008).

6.4 Evidence of heavy metal deposition to soils and biota

6.4.1 Soil composition

The heavy metal content of UK soils forms part of the database on soil composition held in the National Soils Inventory[15] for England and Wales, and by the Macaulay Institute for Scotland. These data represent surveys of surface mineral soils (down to a depth of 15 cm, excluding the litter layer) carried out since the 1970s, and while presenting an overall picture of the spatial pattern across the UK, give little indication of any temporal trends. However, they do include data on 'extractable' metal content, i.e. concentrations likely to be available to biota, as opposed to total metal content, which may not be accessible to biota. The first integrated UK national monitoring programme to include soil measurements was the Countryside Survey, started in 1978. Concentrations of metals in soils were included for the first time in the 2000 survey (Figure 6.7) with repeat sampling in the 2007 survey. The 2000 survey measured the total metal content of 1083

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[15] http://www.landis.org.uk/gateway/ooi/intro.cfm

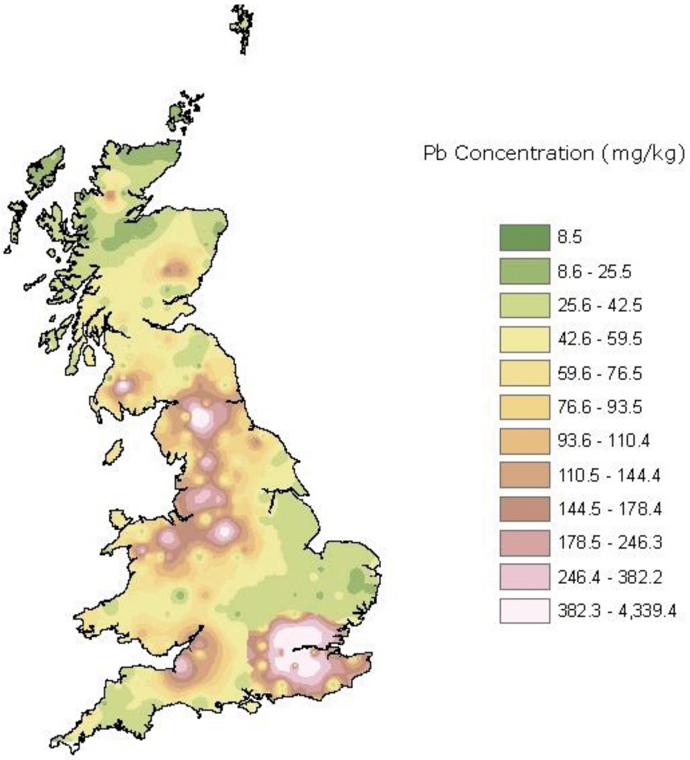

Figure 6.7: Concentrations of total lead (Pb) in surface soil across the UK (compiled using data from the 2000 Countryside Survey).

soil samples from stratified random 1 km x 1 km squares across the UK. 512 plots were resampled in 2007. Concentrations of many of the heavy metals are highly correlated, with two clusters of spatial patterns: lead and cadmium have similar distributions, which are different from another cluster containing chromium, vanadium, nickel, copper and zinc. This correlation may reflect common sources, or physico-chemical properties and behaviour in soils. Additional data on heavy metal spatial distributions is available from the database of stream sediments held by the British Geological Survey[16].

6.4.2 Moss composition from 2005 Moss Survey

Deposition to the UK has been mapped according to the procedure described by Ashmore *et al*. (2002) using the moss calibration (relationship between bulk deposition and concentration in moss) derived by collocated sampling of mosses at the monitoring sites of the rural Heavy Metal Deposition Network (HMDN) in 2004/05 (Fowler *et al.*, 2006). An example deposition map for Pb derived from the 2005 Moss Survey is shown in Figure 6.8 (maps of Zn, As, Cd, Ni, and V are available at http://www.uk-pollutantdeposition.ceh.ac.uk). Figure 6.8 should be compared with Figure 6.6 above for the 2000 Moss Survey. The grid cells in Figures 6.6c to 6.6e reflect the weighted average to the different land cover forms, while deposition to moss represents deposition to short vegetation only. Since the moss deposition fields are referenced to the HMDN, the deposition estimates are not fully independent, although the spatial patterns are independent, and are based on measurements from 170 sites rather than 15 from the rural network. Surveys in 1995, 2000 and 2005 show a consistent decrease in heavy metal content consistent with the decrease in emissions (Harmens *et al.*, 2009).

Both 2000 and 2005 Moss Surveys indicate a large hot spot of As in the south Midlands. The HMDN estimate is different, with hotspots in Wales and the west Highlands. This might indicate that the mosses derive a significant amount of As from wind-blown soil and effectively represent the influence of historical deposition. For Cd, spatial patterns are similar between the different deposition estimates. For Pb, while hot spots are similar in

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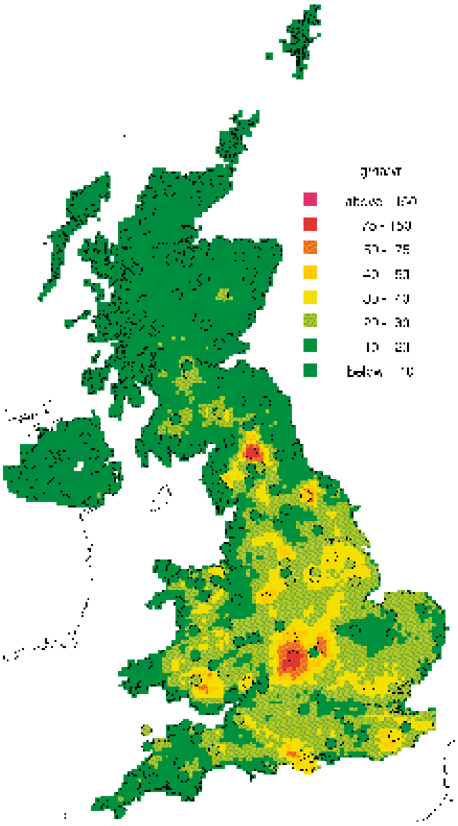
[16] http://www.bgs.ac.uk/gbase/home.html

Figure 6.8: Lead deposition maps (g kg^{-1} y^{-1}) based on the Moss Survey 2005 (cf. Figures 6.6 and 6.7) (Fowler *et al.*, 2006).



the HMDN and 2000 Moss Survey, the 2005 Moss Survey places hot spots near Birmingham rather than Manchester and suggests reduced deposition in South Wales. For Ni, the spatial patterns differ greatly between the two approaches, indicating that Ni concentrations in moss may be affected by wind-blown soil concentrations from historical deposition. The Moss Survey data suggests that V deposition has declined sharply between 2000 and 2004/05, and this later estimate is similar to the HMDN estimate. This decline is not reflected in the NAEI (Murrells *et al.*, 2010). Moss Survey estimates of Zn show little structure because of the relatively weak correlation between concentration in moss and deposition, suggesting that Zn may be more mobile than other metals. The spatial structure between the Moss Surveys in 2000 and 2005 is similar, reflecting mainly the effect of the precipitation patterns. The UK Moss Surveys form part of a wider survey of heavy metals in mosses across Europe conducted under the auspices of UNECE ICP Vegetation[17] (Harmens *et al.*, 2009) which shows the relative concentration in mosses in the UK and the rest of Europe.

6.4.3 Mercury in predatory birds

The Predatory Bird Monitoring Scheme (PBMS)[18] provides a long-term dataset since the early 1960s, based upon the public finding and sending in bird carcases for analysis, and on eggs accepted from licensed egg collectors. These samples are analysed for several persistent organic pollutants and mercury; for mercury in birds of prey there are data for over 3500 samples over 30 years. The data are strongly skewed (e.g. Figure 6.9a), with most of the samples showing low concentrations. However, this spread of data includes variation caused by different factors; statistical analysis showed that the cause of death (starved or other causes), age (juvenile versus adult) and gender (for herons only) play a part in explaining the spread of the data, as well as the date of the sample (Figure 6.9b). In all species there has been a decline in the average mercury content from the 1960s to the present day, with most of the change occurring before 1985 following prohibition of the use of mercurial seed dressings in the early 1970s. However, there are no clear spatial trends across the UK that can be linked to mercury deposition; for sparrowhawks there are several clusters of high concentration in northern and western Scotland, with lower values in southern and eastern England

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[17] http://icpvegetation.ceh.ac.uk

[18] http://pbms.ceh.ac.uk/default.htm

and Wales. There was no increase in concentrations in agricultural areas where mercury seed dressings were formerly used, indicating that current exposure is now more likely to come from global cycling of mercury than from historic local use of seed dressings.

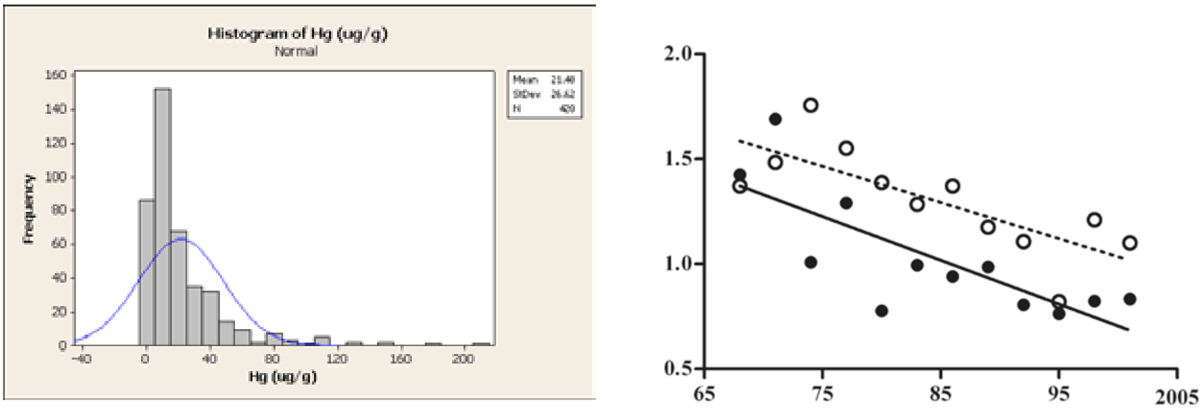


Figure 6.9: (a) Distribution of mercury (µg g^{-1}) in herons and (b) variation over time shown as logarithm of Hg content in µg g^{-1}. Open circles are for starved birds, filled circles for non-starved. (Shore *et al.*, 2006).

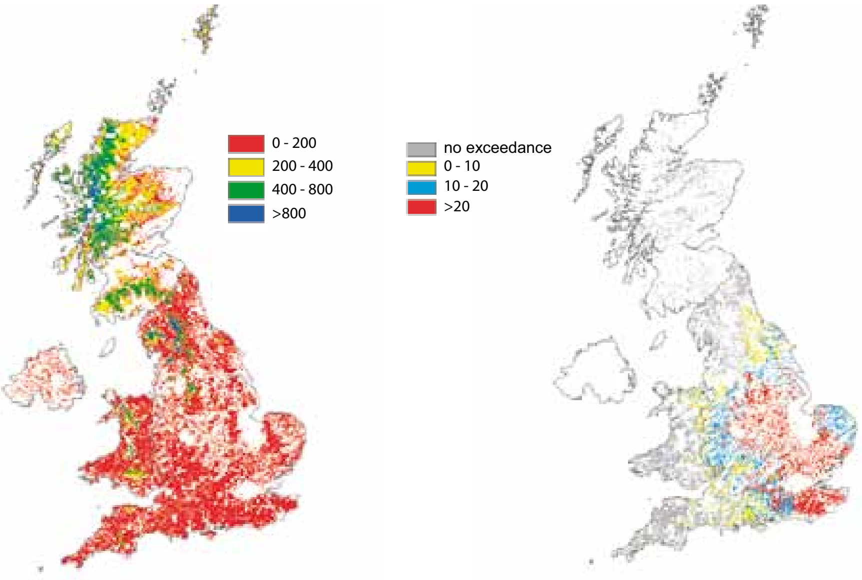
6.5 Critical load exceedances

The cumulative long-term deposition of metals from the atmosphere can have direct impacts on soil and freshwater biota, the long-term sustainability of soils, and indirect effects on human health through the food chain. Assessment of the impacts of metal deposition within the Convention on Long-range Transboundary Air Pollution (CLRTAP) uses the concept of the critical load, i.e. the rate of deposition of metal from the atmosphere which, at steady state, leads to the metal concentration in soils or waters reaching a threshold for adverse effects (a critical limit). In the UK, assessment has focused on critical limits and loads based on the effects of lead and cadmium on soil function – detailed assessments for freshwater and for the effects of mercury have not been undertaken. Assessments have also been made for copper, zinc and nickel. Methodologies have generally followed those in the CLRTAP Mapping Manual (UNECE, 2004); a more detailed description of their application in the UK is provided by Hall *et al.* (2006c).

First, the critical limit (at which significant adverse ecological effects occur for the metal of interest) is calculated as the pH-dependent concentration of the free metal ion in soil solution (Lofts *et al.*, 2004) at which 95% of organisms are protected. The toxicity data used to define this value are based on effects on microbial processes, plant roots and soil invertebrates. These critical limits are then compared with measured pH and total concentrations of metals in soils. The next stage is to calculate the critical load at steady state, i.e. when the rates of input and output of metal balance, at the critical limit. Finally, the steady-state critical load is compared with the current rate of deposition to determine areas of critical load exceedance. Several possibilities exist for a particular site and metal: both the critical limit and the critical load may be exceeded (i.e. there is a current risk of harm and current deposition rates increase the risk), neither may be exceeded (no current or likely future risk), the critical limit may be exceeded, but not the critical load (a current risk of harm from soil minerals or historic deposition, likely to diminish with time), or the critical load may be exceeded but not the critical limit (no current risk of harm, but implying that the critical limit will be exceeded, and risk of harm will increase, at some unspecified future time). The estimation of the timescales within which critical load exceedances result in actual risks to biota is addressed through dynamic modelling (see below).

Critical loads are calculated in the UK for Cd, Pb, Cu, Ni and Zn, for the following six habitats: grassland (acid and calcareous), heathland, bog, managed coniferous woodland, managed broadleaved woodland and unmanaged woodland. Critical loads and their exceedances are then mapped across the UK using data on land cover (the six habitat classes), soil pH and organic matter, dissolved organic carbon, annual run-off (to estimate the leaching flux), metal uptake (by managed woodland), soil metal concentrations and heavy metal deposition. In the UK, critical loads for metals are assessed only for ecosystem effects. As an example, the minimum critical load for lead is shown in Figure 6.10, alongside the map of critical load exceedance for managed broadleaved woodland. Maps of critical load exceedance for other metals and habitats may be found at www.rotap.ceh.ac.uk. In general, the lowest critical loads are found in the south and east of the UK, and the higher values in the north and west. This reflects the national pattern of the leaching of metal from soil, which is higher in areas with higher rainfall and run-off. In the south and east, where leaching rates are lower, metal is likely to be retained in the soil for longer and hence the critical load is lower than in the north and west. Based on 2005 deposition data, there is no exceedance for any habitat for Ni and virtually no exceedance for Cd. There is very little exceedance of Cu, Pb and Zn critical loads for non-forest habitats and for managed coniferous woodland (Table 6.3). However, critical loads over 50% of the areas of managed broadleaved woodland and unmanaged (coniferous and broadleaved) woodland were exceeded for Cu, Pb and Zn, implying the risk of harm at some unspecified future date. It takes a long time for concentrations of Pb in soils to build up to levels at which free Pb ions in soil solution exceed critical limits, hence the critical load for this metal is exceeded in large areas of broadleaved and managed forest in the UK but this does not imply that there is an immediate threat to the functioning of these soils.

Figure 6.10: (a) Minimum critical load for lead (g ha^{-1} yr^{-1}) and (b) exceedance of critical load for lead in managed broadleaved woodland (Ashmore *et al*., 2007).



Despite the exceedance of critical loads for Pb, there is virtually no exceedance of its critical limit for any habitat (Table 6.4). Conversely, although there are virtually no exceedances of critical loads of Cd, there are areas of critical limit exceedance for all habitats. Critical limits for Ni, like critical loads, are not exceeded. Exceedances of the critical limit for Cu extend across England and Wales, with significant areas of exceedance for broadleaved and unmanaged woodland. The areas of critical limit exceedance for all habitats are highest for Zn. Figure 6.11 shows the spatial distribution of critical limit exceedance for Cu and Zn. It is important to note that exceedance of critical limits may reflect geological and other sources, and not simply the effect of atmospheric deposition. For example, the high exceedance of critical limits for Cu in Northern Ireland can be attributed to known geological sources. In contrast to critical load exceedance, critical limit exceedance is found throughout England and Wales, although it is less frequent in northern England and Scotland. The main reason for the different patterns of critical limit and critical load exceedance is likely to be the different rates of change in soil metal pools in relation to changes in metal deposition. Critical limit exceedance provides an indication of the current soil status. Critical load exceedance provides an indication of areas potentially at risk when steady state is reached.

Countryside Survey data have also been used to establish the proportions of sites for which metal contents exceed the critical limit for harmful effects to biota (Spurgeon *et al.*, 2007). The greatest risk appears to come from zinc, for which over 43% of samples had calculated pH-dependent soluble zinc concentrations above the critical limit.

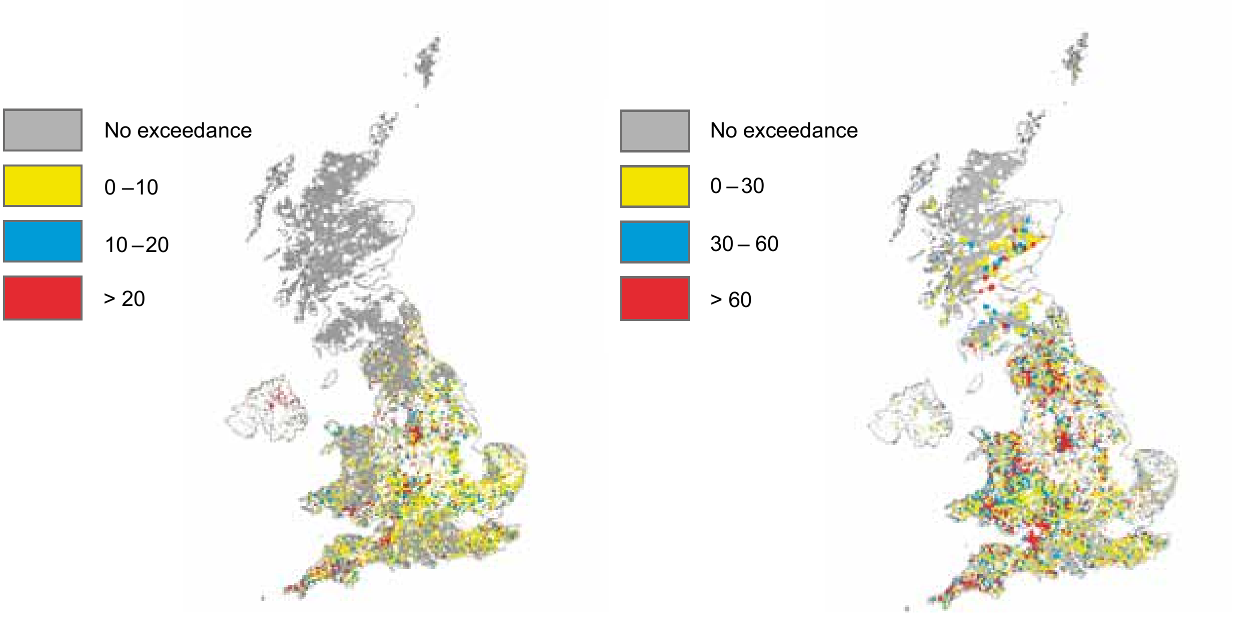


Figure 6.11: Maximum critical limit exceedance for (a) Cu and (b) Zn (g ha^{-1} yr^{-1}) Source CEH/ RoTAP.

Table 6.3: UK critical load exceedances by habitat and metal based on 2005 data (Ashmore *et al*., 2007).

UK habitat	Percentage area habitat critical load exceedance for:				
	Cd	Cu	Ni	Pb	Zn
Grassland	none	8%	none	3%	9%
Heathland	none	<0.01%	none	0.1%	0.1%
Bog	none	<0.01%	none	None	0.1%
Managed conifer	<0.001%	6%	none	11%	6%
Managed broadleaved	none	50%	none	62%	58%
Unmanaged woodland	none	50%	none	58%	54%

Table 6.4: Exceedances of critical limits by habitat and metal across England and Wales data (Ashmore *et al*., 2007).

UK habitat	Percentage area habitat critical limit exceedance for:			
	Cd	Cu	Pb	Zn
Grassland	8%	18%	1%	44%
Heathland	5%	2%	1%	26%
Bog	1%	1%	0.5%	26%
Managed conifer	6%	8%	0.2%	36%
Managed broadleaf	9%	50%	1%	56%
Unmanaged woodland	10%	42%	1%	53%

6.6 Dynamics of heavy metals in terrestrial and freshwater ecosystems

The accumulation and release of Ni, Cu, Zn, Cd and Pb in catchments for which atmospheric deposition is the main heavy metal input has been assessed using the process-based catchment model CHUM-AM (Tipping *et al.*, 2006a; Tipping *et al.*, 2006b). The calculations are based on soil properties, chemical weathering, rainfall and the long-term (several hundred years) history of atmospheric deposition, of both metals and acidifying compounds. The model can reproduce, to within a factor of 3, observed contemporary soil metal pools and streamwater concentrations for 11 study catchments (Ashmore *et al.*, 2004; Ashmore *et al.*, 2007; Tipping *et al.*, 2006b; Tipping *et al.*, 2007). Comparison of the current values with pools and concentrations estimated for 'pristine' conditions indicates appreciable heavy metal enrichment due to cumulative atmospheric deposition. Enrichment varies considerably among catchments but is typically five-fold for Ni and Cu, and 20-fold for Zn, Cd and Pb. The principal control on these heavy metals is binding by soil organic matter, which is strong for Cu and Pb, but weaker for Ni, Zn and Cd. Because of the large capacity of soil organic matter for metal binding, varying acidification status and changes in metal deposition rates over time, the soils are not in steady state with respect to heavy metals.

CHUM-AM was run with different scenarios to examine how future heavy metal behaviour will depend upon metal deposition, nitrogen and sulphur deposition, and losses or gains in soil organic matter (Ashmore *et al.*, 2007) in five catchments. For the scenario considered most likely, the toxic threats of Cd in soil and water are forecast to decrease or remain steady in three catchments, while those of Pb show both increases and decreases. The results of our analysis and modelling suggest that the full environmental benefits of the reductions in emissions and deposition of metals over the past 30 years may only be felt over long timescales which vary according to the metal. Specifically, further reductions in the deposition of Ni, Zn and Cd would have widespread beneficial effects, in terms of soil and water concentrations, during the 21st century; beneficial effects cannot be expected for Cu and Pb, except over much longer timescales; it is important to ensure that metal deposition does not rise, and that soil organic matter is protected. Further assessments of critical loads, critical limits, and dynamics in soils and waters in the UK are required for Hg, the third priority metal within CLRTAP, in addition to Pb and Cd.

Currently policy assessment within CLRTAP has focused on the costs and effectiveness of additional measures to further reduce emissions of lead, cadmium and mercury, but only considers benefits in terms of critical load exceedance for these metals. Our analysis shows these additional measures also need to be considered in terms of (i) critical limit exceedance, and hence actual impacts, which may be quite different from critical load exceedance, and (ii) the timescale of response to emission reductions, which may be very long.

6.7 Modelling of emissions, transport and deposition

A detailed description of atmospheric transport models is given in Chapter 4 and Appendix B. The results of European-scale modelling of heavy metals with the EMEP model and UK-scale modelling with FRAME are discussed here. The FRAME model was run for the UK at 5 km resolution with emissions input from the official UK National Atmospheric Emissions Inventory (NAEI) for the year 2005 using boundary conditions from a European-scale simulation. The deposition and air concentration were calculated for As, Cd, Cr, Cu, Ni, Pb, Se, V and Zn. The EMEP model was run for Europe at a 50 km resolution using emissions data from the ESPREME project[19] for Cd, Hg and Pb. Here we consider the concentrations of Pb in air. Modelling atmospheric Hg is described below, and a summary comparison of UK official emissions and measured and modelled deposition budgets is shown in Table 6.2. The Pb concentrations interpolated from the monitoring network, Figure 6.12a, are found to be larger than those modelled with FRAME, Figure 6.12b, by an order of magnitude. Differences in spatial patterns occur because FRAME is linked to spatially disaggregated emissions sources. For example, a hot spot of high Pb concentrations is evident from the model in South Wales but is not represented by interpolation of measurements from the rural monitoring network. The official UK emissions estimates used in the model are insufficient to explain the measured concentrations, as noted above. Concentrations of Pb modelled within EMEP (Ilyin *et al.*,

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[19] http://espreme.ier.uni-stuttgart.de

2008) show better agreement with measurements due to use of the ESPREME emissions inventory and the inclusion of resuspension of metal particles from land. ESPREME emissions of Pb for the UK for 2000 were 570 tonnes compared with only 160 tonnes from the NAEI.

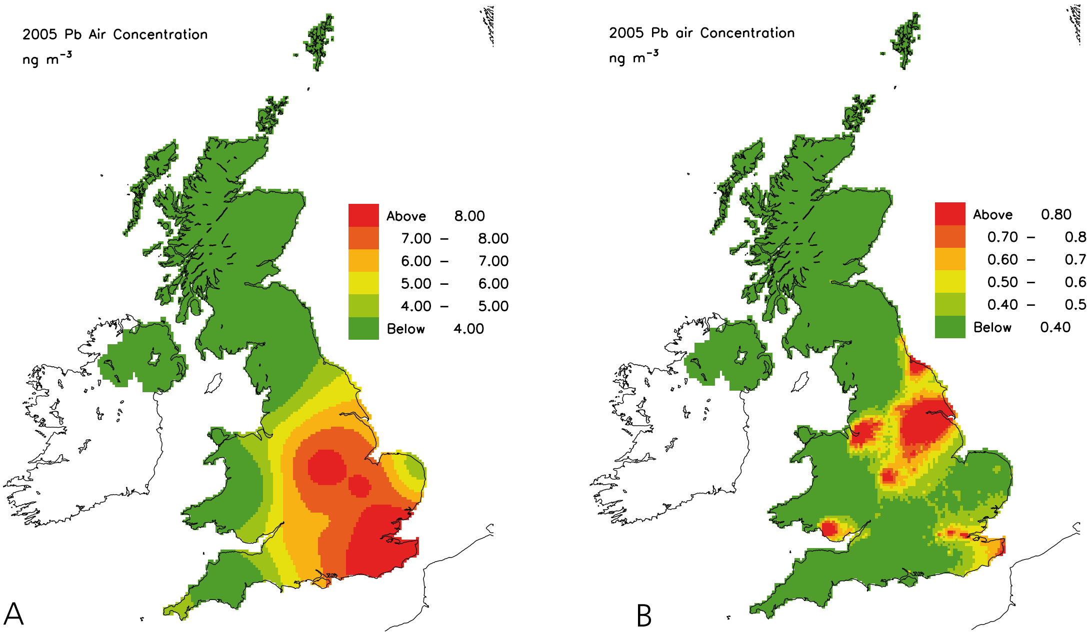

Figure 6.12: Pb concentrations in air (ng m^{-3}) (a) Interpolated from the UK monitoring network (Fowler *et al*., 2006); (b) Calculated with FRAME using NAEI emissions (Note factor of 10 difference in scales between (a) and (b)).

ESPREME and official estimates showed large differences in emissions from industrial processes and gasoline combustion in mobile sources. The contribution of wind-driven resuspension to air concentrations of Pb and Cd in the EMEP model was similar to emissions from primary sources. These results show that inclusion of both resuspension and comprehensive emissions estimates in national-scale modelling is necessary to reproduce measured concentrations and deposition. The EMEP model was used to assess the contribution of emissions from different countries to deposition of Pb in the UK and demonstrated that the primary source (59%) is associated with emissions from the UK.

Several models have been built to address the fate and behaviour of mercury emissions (Ryaboshapko *et al.*, 2007a; Ryaboshapko *et al.*, 2007b; Ryaboshapko *et al.*, 2002). In Europe, the most important model for mercury policy development is the MSC-East mercury model (Ryaboshapko *et al.*, 1999), a regional- and hemispheric-scale model adopted to underpin the UNECE Heavy Metals Protocol. In the UK, a mercury scheme has been incorporated into the global Lagrangian chemistry–transport model STOCHEM to assist Defra in its air quality policy formulation. Figure 6.13a presents the European-scale deposition field for mercury from the MSC-East model (Ilyin *et al.*, 2005). Highest deposition levels are found in Germany, Poland and Ukraine, reaching over 50 g km^{-2} yr^{1}. Deposition levels over the UK appear to be similar to those modelled over the remainder of north-west Europe and are of the order of 10-20 g km^{-2} yr^{-1} over much of central UK. Figure 6.13b presents the detailed model deposition field for the UK for 2006 showing the presence of a deposition maximum of 51 g km^{-2} yr^{-1} in north-west England and lower levels in the north and west of the British Isles with a deposition minimum of under 5 g km^{-2} yr^{-1}. Much of the deposition to the UK is driven by the global mercury circulation which accounts for about one half of the total mercury deposition budget. The other half arises from man-made emissions within Europe. UK emissions are responsible for the bulk of the UK deposition of man-made mercury.

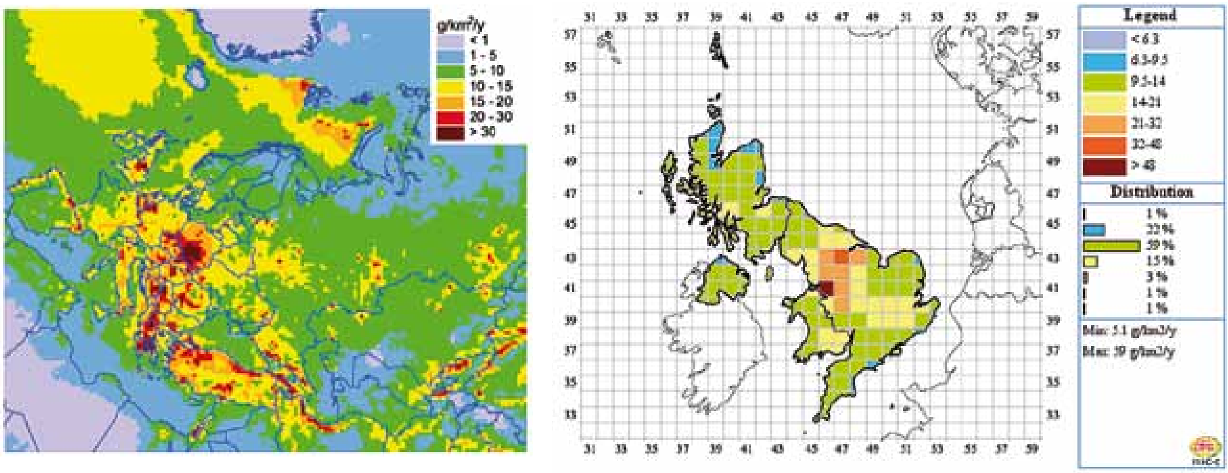

Figure 6.13: (a) The deposition field for mercury from the MSC-East model for 2003 (Ilyin *et al.*, 2005); (b) The deposition field for mercury (g km^{-2} yr^{-1}) across the British Isles from the MSC-East model for 2006 (Gusev *et al.*, 2008).

There are many uncertainties in the current understanding of the environmental fate and behaviour of mercury and hence in the atmospheric models employed to describe them. Problems arise because of the inadequacies and uncertainties in the chemical kinetic data employed to describe mercury transformations (Calvert and Lindberg, 2005). In regional models, calculated mercury concentrations are found to be linearly dependent on the boundary conditions (Pongprueksa *et al.*, 2008). In global models, calculated deposition outweighs emission to such an extent that it is not possible to reproduce the observed hemispherical background concentration levels without employing empirical re-emission factors (Selin *et al.*, 2008). Model performance is not completely satisfactory for a model considered as 'state of the art' for policy formulation across Europe.

6.8 Case study: Heavy metals in the Lochnagar catchment

The Lochnagar catchment is part of the Defra-funded UK Acid Waters Monitoring Network (AWMN), in which trace metal analyses were undertaken on sediment trap material at 11 lakes, and on catchment mosses and selected aquatic plants at all 22 lake and stream sites annually from 1997 through to the cessation of funding for this aspect of the AWMN in 2006. These data showed that sediment quality guidelines for Hg (MacDonald *et al.*, 2000) were regularly exceeded in all areas of the UK. More detailed trace metal monitoring at Lochnagar (Tipping *et al.*, 2007) included multiple sediment and soil core analyses to obtain decadal inventories for the full catchment and lake basin (Yang *et al.*, 2001; 2002b; 2002c); fortnightly monitoring of Pb, Cd, Cu, Ni, Zn in bulk deposition and lake water and monthly monitoring of Hg; fortnightly monitoring of methylmercury in deposition and lake water, and annual monitoring of trace metals in a number of ecological compartments including catchment and aquatic plants, zooplankton and sediment trap material (Yang *et al.*, 2002a). Mercury in fish from Lochnagar has also been shown to be elevated when compared with other European mountain lakes (Rosseland *et al.*, 2007). Annual volume-weighted deposition of trace metals at Lochnagar showed a general decline over the monitoring period in agreement with trends in many of the biotic parameters, particularly the aquatic and catchment plants. By contrast, the full sediment basin inventories for Pb and Hg showed no decline in total inputs since the 1970s, the period over which a dramatic decline in metal emissions and deposition occurred in the UK (Yang *et al.*, 2002b). This 'additional' input can only come from previously deposited trace metals deposited and stored in the catchment and now being released to the loch. The EU-funded project *Euro-limpacs*[20] (2004-2009) has explored this at nine further sites across Scotland and has shown that this enhancement is mainly due to metal inputs as a result of erosion of organic catchment soils. Predicted climatic changes that enhance soil erosion (drier summers, wetter winters, more severe 'events', etc.) may therefore exacerbate the transport of catchment-stored trace metals to upland waters despite emissions reductions (Rose *et al.*, 2004). For Lochnagar, Yang *et al.* (2002b) predicted that over 400 years worth of deposition (at 2000 levels) are stored in the Lochnagar catchment indicating a massive potential for metal release. The Euro-limpacs project indicates that this is a widespread phenomenon across Scotland and that 'recovery' from trace metal contamination could be significantly delayed as a result.

In addition to the work at AWMN sites a number of projects have generated dated sediment profiles (concentration and flux) for over 40 lakes across the UK. These data can be used to assess temporal trends in trace metal inputs at an individual site (e.g. (Yang and Rose, 2005) providing a means to assess direction (improvement or deterioration) as well as rates of change. Further, the data from lakes can be used as a spatial array of sampling points thereby indicating contamination patterns across a broader region. For example, more than a quarter of the sites in London have Hg concentrations above 560 ng g^{-1} in surface sediments, above the 'apparent effects threshold' at which biological effects have always been observed (MacDonald *et al.*, 2000), and which indicates significant and widespread contamination. UK lake sediments have also been used in a Tier 1 Sediment Ecological Risk Assessment to assess the impact of trace metals at ambient concentrations on chironomid survival and emergence and cladoceran survival and reproduction (Rippey *et al.*, 2008). The results showed that around half of the studied lakes were at least moderately contaminated by Pb, Zn and Cd while the toxicity quotient indicated Pb as the trace metal of concern (along with As and polyaromatic hydrocarbons (PAHs)). This toxicity work is now being extended to include an additional nine lakes as part of the OPAL project, which has initiated a trace metal monitoring programme at one lake in each of nine regions of England.

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[20] http://www.refresh.ucl.ac.uk/eurolimpacs

6.9 Human health and long-term trends

The Expert Panel on Air Quality Standards (EPAQS, 2008) recommends guideline values for metals classified as human or suspected human carcinogens which have been shown to affect human health through inhalation. The values, based upon the PM_{10} fraction annual mean are 3 ng m^{-3} for total inorganic arsenic, 20 ng m^{-3} for total nickel compounds, 0.2 ng m^{-3} for total particular beryllium compounds and 0.2 ng m^{-3} for chromium compounds in the Cr(VI) oxidation state. The report includes data on the concentrations of As, Cr and Ni in rural air from 1957 to 2005. The long-term trends in concentrations of these and other heavy metals are shown in Figure 6.14, based on data from rural measurements (Brown *et al.*, 2008; Cawse, 1987; Lee *et al.*, 1994; Salmon *et al.*, 1978). It is clear (note the logarithmic scale on the vertical axis) that air concentrations of all metals in rural air have fallen by more than a factor of 10 over the past 50 years, to the point where in rural air they do not pose a human health risk.

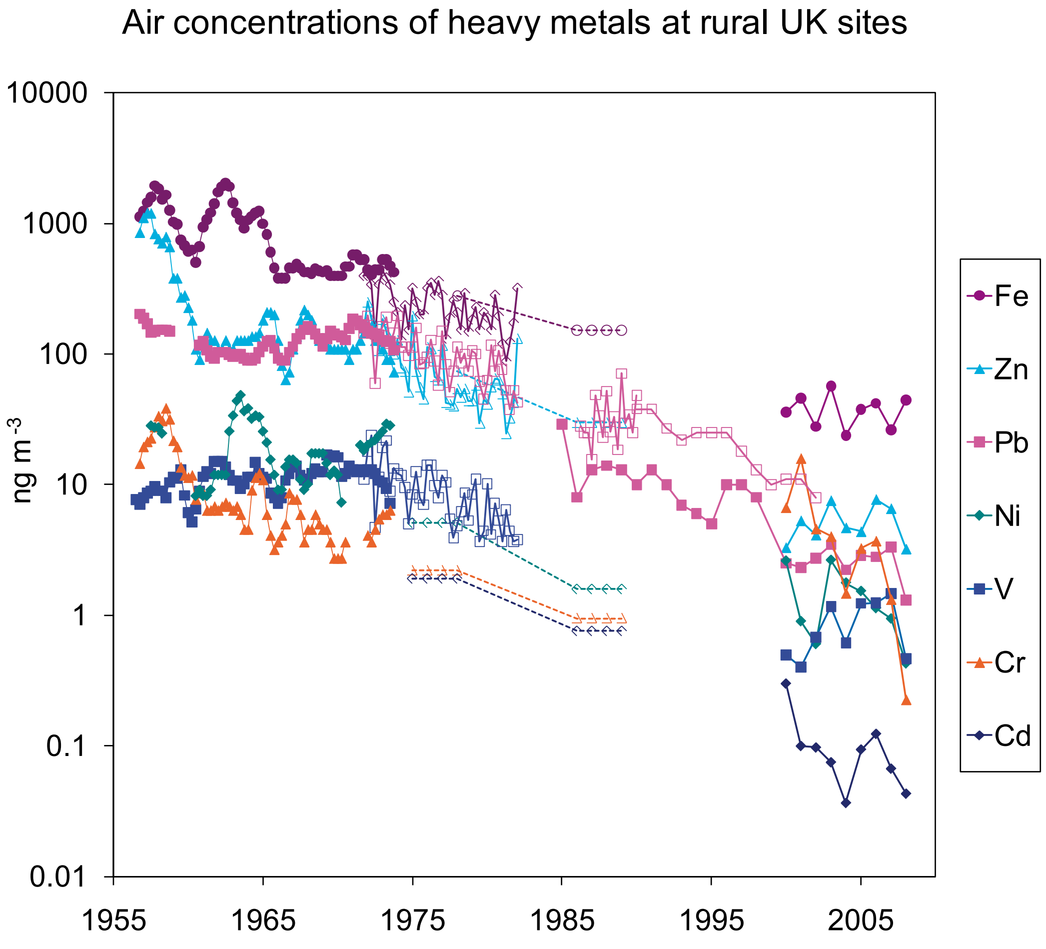

Figure 6.14: Concentrations of particulate metals in UK rural air from 1957 to 2007 (Note logarithmic vertical scale.) pre 1974 at Chilton (closed symbols) (Salmon *et al.*, 1978); 1972-1981 at Chilton (open symbols)(Cawse, 1987); 1970s to 1980s at Chilton and Windermere (open symbols)(Lee *et al.*, 1994); 1985-2003 Pb at Chilton (open symbols) and Eskdalemuir (closed symbols) (Brown *et al.*, 2009) and 2000-2008 at Eskdalemuir (Brown *et al.*, 2009).

6.10 Discussion

The establishment of a rural monitoring network for measuring heavy metal concentrations in air and precipitation has demonstrated that measured deposition across the UK is much greater than can be accounted for by current official emissions estimates. Processes such as fugitive emissions from industry and resuspension by wind and mechanical distrurbance may account for the difference, but too little is known quantitatively about these processes. This problem is not unique to the UK; increased scientific knowledge would be applicable worldwide.

Concentrations of heavy metals in air as particulate matter (PM) do not currently exceed guidelines for human health in rural air, but there are few data to quantify the risks in urban areas, especially where resuspension from traffic may be an important secondary source. Current rates of deposition cannot be used to judge actual or potential effects on ecosystems remote from individual point sources without knowledge of the existing soil conditions. Historic deposition patterns have left a legacy of heavy metals in soils, currently locked up by soil organic matter. However, in some places (often with input from underlying rock weathering) current levels of heavy metals in soil produce bioavailable concentrations in solution which pose a risk to biota. This risk, estimated by the use of critical limits, is more important for assessing current threats from heavy metals to biota than critical loads, which are relevant at ‘steady state’, and which may not be achieved for centuries.

The release of heavy metals from a bound form in soil into solution and into freshwaters appears to depend on the availability of and changes in soil organic matter and soil pH; changes in soil composition as a result of changes in climate, or mechanical disturbance, may release the stored material in a bioavailable form, and this is one of the largest uncertainties when considering the impact of future climate on heavy metals in the UK environment.

Chapter 7 European and Global Perspectives

Summary

- European emissions of sulphur dioxide have continued to decrease and with current policy agreements will continue to decrease over the next 10-15 years. By 2020 emissions will be less then 10% of those in 1980.
- European emissions of nitrogen oxides (NO_x) are also decreasing and by 2020 will be reduced by about 70% compared to those in 1990.
- For ammonia, emission reductions have been small. The emissions in 2020 will be reduced by approximately 40%.
- Emission reductions have substantially improved European air quality. Concentrations of sulphur dioxide across Europe are a small fraction of values 20 years ago. They have also reduced exceedances of critical loads and levels. The ongoing reductions will further improve the situation, with particular respect to acidification. For eutrophication, reductions are smaller and there will still be large exceedances by 2020 indicating a need for further significant reductions in atmospheric emissions of ammonia and nitrogen oxides.
- The relative importance of emissions from shipping has increased over the last decades and significant reductions are needed to meet critical loads and levels. Recently agreed emission controls on sulphur dioxide will significantly improve the situation but under the current regulatory system, it is projected that NO_x emissions from shipping will remain at similar levels to those evident today. This is a priority target for governments to address.
- UNECE and EU strategies to control emissions of NO_x and volatile organic compounds (VOCs) led to reductions in peak ozone concentrations and improvements in air quality. However, ozone concentrations large enough to damage human health and vegetation are still common and substantial problems remain throughout Europe, especially in warm summers such as 2003. In part the problems require further reductions of the ozone precursor gases within Europe, but to be fully effective in protecting human health and ecosystems in Europe, emission reductions over a much larger geographical scale (i.e. hemispheric) are required.
- Current capability to characterise and model air pollution–climate change feedbacks is immature, due to the complexity of the system and the lack of work in this area.
- Changes in transboundary transport of pollution as a consequence of climate change are small relative to the climate change impact on air pollution emissions. Further general statements would be premature at this stage.
- Intercontinental transport and transport of pollutants from sources outside the European continent have become more important as emissions in Europe have decreased. North Atlantic shipping emissions and North American emissions are of particular importance for European air quality.

7.1 Introduction

Assessment of regional and transboundary air pollution has a history of about 40 years. The first observations leading to systematic scientific analysis and policy interest were made in the late 1960s. The observations formed a basis for the first policy-driven study coordinated by the Organisation for Economic Co-operation and Development (OECD, 1977). The study, directed at the transport of sulphur over western Europe, concluded that there was significant transport of pollutants across borders in Europe and that no country was in the position to solve domestic air pollution problems simply by controlling emission within their national boundaries. The study formed the basis for wider interest, namely the establishment of the 'Co-operative programme for monitoring and evaluation of the transmission of air pollutants in Europe' (EMEP) in 1977, and later the UN Economic Commission for Europe (UNECE) Convention on Long-range Transboundary Air Pollution (CLRTAP) signed in 1979.

The Convention has been successful in terms of policy achievements, and large emission reductions have been achieved through its protocols. Looking back on 30 years of work, the Convention has developed a comprehensive system of initiatives, processes and centres that have driven not only agreements under the Convention but also the development of common air pollution policies within the European Union and to a large extent national air pollution initiatives. More recently the scope of the Convention has widened from European air pollution to include intercontinental transport of atmospheric pollution and emissions from shipping.

As emission reductions have occurred in Europe, emission sources outside Europe have become more important for European air quality. This is particularly true for North American and North Atlantic emissions. The increasing interest in the larger scale initiated the formation of a separate activity under CLRTAP, the Task Force on Hemispheric Transport of Air Pollution.[21] Emissions from shipping have received increasing interest from international bodies, which most recently resulted in a decision by the International Maritime Organization on emission reductions for sulphur dioxide and nitrogen oxides.

Rapid industrial development and urbanisation in other parts of the world have also increased air pollution problems, in particular in south and east Asia. The transboundary nature of these problems has been the basis for regional initiatives such as the Male Declaration[22] and the EANET[23] (Acid Deposition Monitoring Network in East Asia). Both of these initiatives have brought countries together in monitoring and evaluation programmes and also in discussion on emission control.

European air pollution policies are in continuous development. To further improve air quality in Europe, in 2005 the European Commission launched a Thematic Strategy on Air Pollution (CEC, 2005) with the aim of further improving air quality by 2020. The Strategy proposes guidelines for the protection of human health, but also for the protection of ecosystems, and in 2008 the EU agreed relevant air quality guidelines. A revision of the

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[21] Task Force on Hemispheric Transport of Air Pollution (TFHTAP), http://www.htap.org/

[22] http://www.rrcap.unep.org/male/baseline/indexpak.html

[23] http://www.eanet.cc/

National Emission Ceilings Directive (NECD) (CEC, 2001b) is currently under negotiation, with the aim of further reducing emissions of sulphur dioxide, nitrogen oxides, ammonia, volatile organic compounds and particles. In addition to the NECD, the European Energy and Climate Package will further reduce emissions of those pollutants considered in this report. The consequences of proposed EU legislation on emissions will be further discussed in relation to each of the compounds concerned. The CLRTAP revision is expected to go one step further in reducing the impact of transboundary air pollutants and meeting criteria for critical loads and levels, and air quality. The CLRTAP revision will include more countries than the NECD.

In all the work under CLRTAP, science, monitoring and modelling have played a crucial role. Shared efforts through the Convention have formed a strong infrastructure supporting countries in their development of air pollution policies to an extent far beyond what single countries can achieve by themselves. In this work the UK has taken a strong position both with respect to the development of scientific knowledge but also through taking responsibility for developing and maintaining international collaboration.

In this chapter, the wider perspective of air pollution in relation to the assessment of the UK situation is presented. The chapter considers both European and wider international aspects of transboundary pollution issues including intercontinental transport and hemispheric air pollution.

7.2 Trends in emissions, concentrations and deposition over Europe 1980-2007

7.2.1 Sulphur

European sulphur dioxide (SO_2) emissions have continued to decrease during the first decade of the 21st century. In 1980 SO_2 emissions from the EU27 were 39.3 million tonnes. In 2005 these emissions were down to approximately 8.3 million tonnes, a reduction of 79%, and are now at levels typical for the end of the 19th century (Figure 7.1). Emissions are expected to decline further in line with existing or proposed legislation and by 2020 they are estimated to be approximately 2.9 million tonnes (Amann *et al.*, 2008). Compared to 1980, emissions will be reduced by more than 92%. Air pollution policy on sulphur dioxide has been successful and is largely complete. Achievements in almost all countries are much larger than was foreseen at the signing of the Gothenburg Protocol in 1999. There are several reasons for these emission reductions. Some were delivered through changes in the fuels used in power generation and heating, including the replacement of coal with natural gas, nuclear power and biomass, and some arose through the use of flue gas desulphurisation units. The closure and transition of industries in eastern Europe have also been of great importance. Globally the decine in sulphur emissions in Europe has coincided with large increases in emissions in China, some fraction of which can be attributed to the manufacture of goods destined for Europe.

Since the UK is part of the European Union, it is of interest to analyse the extent to which UK emission reductions match those of the EU as a whole. In Figure 7.2 the trends in emissions between 1990 and 2006 are shown for the UK, the other countries within the European Union signing the NECD (EU15 excluding the UK), and those countries entering the European Union in 2004 (EU25-EU15). It is striking to see how similar the developments have been for the three groups of countries. However, it is also clear that the reductions achieved in the UK exceed those in the EU 15 and in the EU25-15, a notable achievement. It would be reasonable to expect reductions for the new Member States to have been larger than for the rest of Europe due to the rapid change in the situation after 1990 but this is not the case.

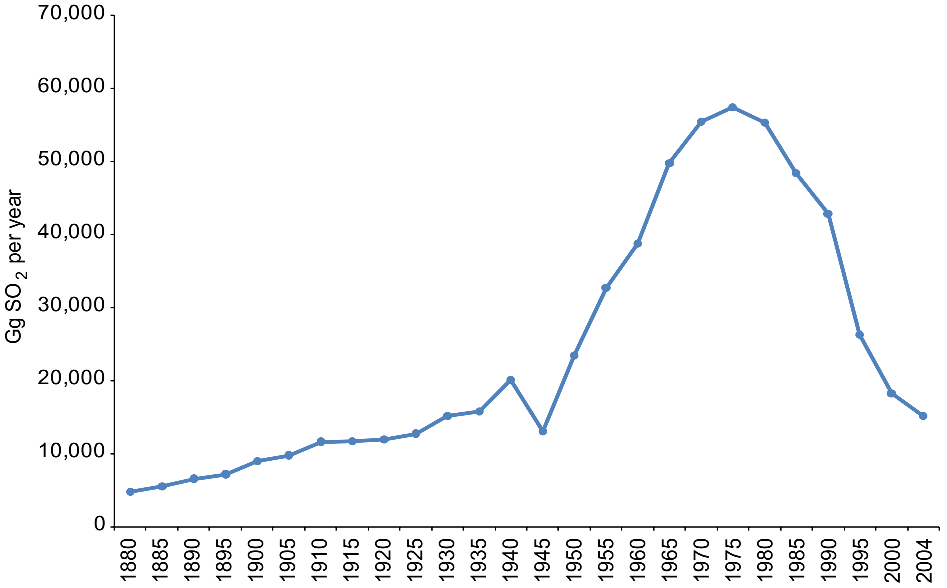

Figure 7.1: Historical emissions of sulphur dioxide in Europe in Tg SO_2 (Vestreng *et al.*, 2007).

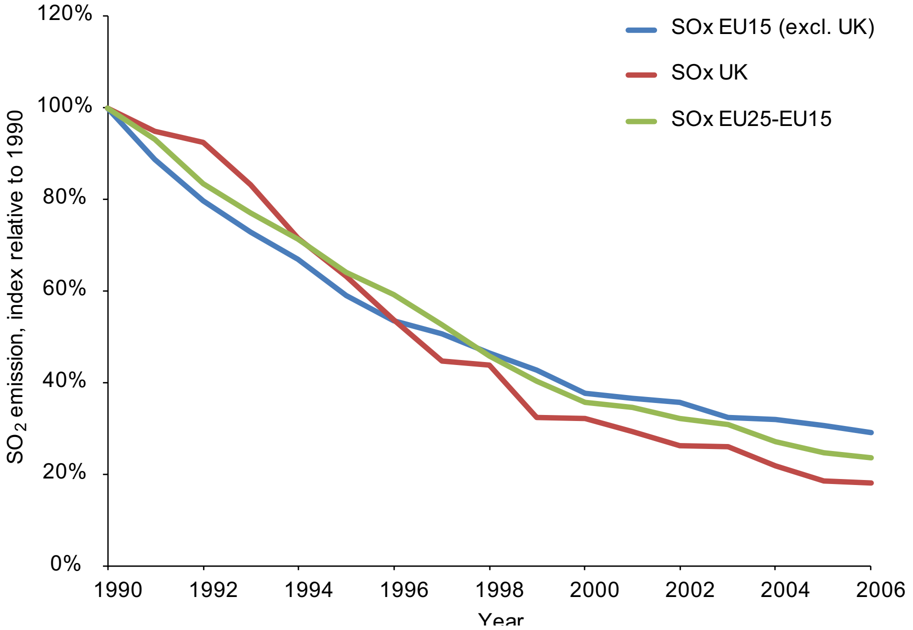

Figure 7.2: Emissions of sulphur dioxide in the UK, EU15 (excluding the UK) and EU25-EU15 between 1990 and 2006.

Atmospheric concentrations and deposition

The favourable development in emissions reductions can be compared with monitoring data for sulphur compounds in air and precipitation. Trends in air concentrations of sulphur dioxide are shown in Figure 7.3. The figure shows that decreases in SO_2 concentrations started in the 1980s and that there has been an ongoing decrease in concentrations ever since. An evaluation of data from all EMEP monitoring sites indicates that sulphur dioxide concentrations were reduced by between 50% and 90% between 1980 and 2000 (EMEP, 2005).

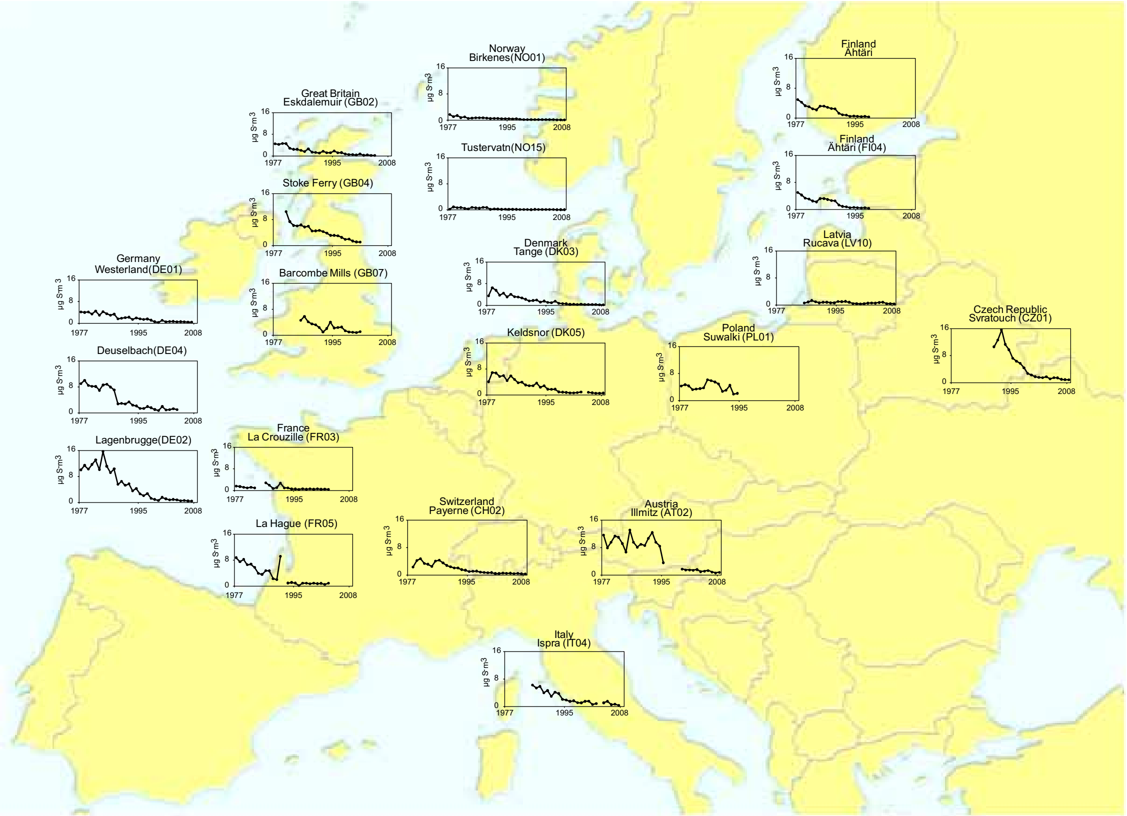

Figure 7.3: Trends for SO_2 concentrations in air between 1978 and 2009 at a number of European EMEP sites with long data series (Source: EMEP monitoring database available at http://tarantula.nilu.no/projects/ccc/emepdata.html).

Concentrations of particulate sulphur have not declined as rapidly or to the same level as sulphur dioxide. A comparison of percentage reductions in concentrations for a number of European countries with long-term datasets shows that reductions in sulphate are typically 10-20% smaller than those for sulphur dioxide (Table 7.1). In fact, the reduction in sulphur dioxide concentrations are larger than the emission reductions over the same time in some areas, while reductions in sulphate (SO_4^{2-}) are smaller, indicating that there is a change in the SO_2/SO_4^{2-} ratio over the same time (Figure 7.4). These trends are similar to those shown for the UK in Chapter 3, and the non-linearities have the same cause (Fowler *et al.*, 2005). The change in ratio is illustrated by data from a Danish monitoring station but is similar to those observed over the UK.

Table 7.1: Changes in measured sulphur dioxide and particulate sulphate concentrations in relation to emission reductions in the period 1980-2000.

Country	Decrease in emissions	Decrease in observed SO_2	Decrease in observed particulate SO_4^{2-}
Austria	90%	85%	70%
Belarus	80%	60%	50%
Czech Republic	85-90%	80%	50%
Denmark	90%	90%	70%
Finland	85-90%	85-90%	60-70%
France	80%	85-90%	50-60%
Germany	90%	90%	70%
Italy	75%	70-75%	50%
Latvia	85%	75%	75%
Lithuania	85%	80%	75%
Norway	80%	70-85%	50-70%
Poland	60-65%	65-80%	60-70%
Slovak Republic	85%	65%	50-65%
Switzerland	80-85%	90%	75%
Sweden	85-90%	85-90%	70-75%
United Kingdom	90%	85-90%	50%

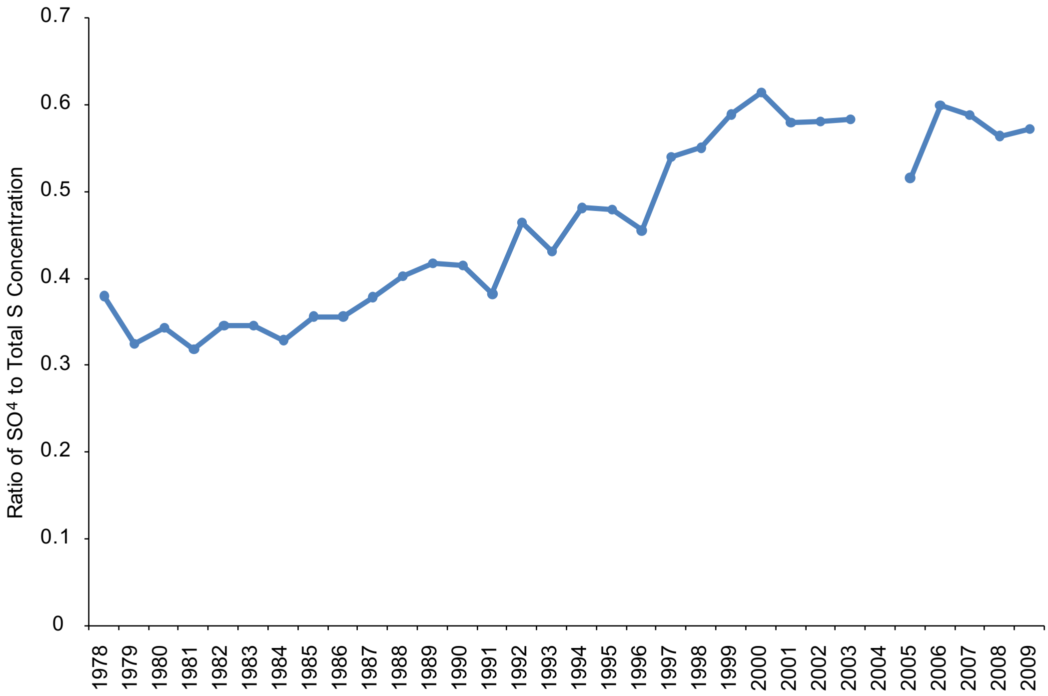

Figure 7.4: Time series for the ratio between annual sulphate in air and the annual total sulphur concentration (sulphur dioxide plus particulate sulphate) at the Keldsnor site in Denmark (EMEP Site DK05) 1978–2009. (Source: EMEP monitoring database available at http://tarantula.nilu.no/projects/ccc/emepdata.html).

The EMEP model is used to generate source–receptor tables of deposition of oxidised sulphur (SO_x) and oxidised (NO_y) and reduced nitrogen (NH_x) for each of the countries in Europe, and of the proportion of deposition associated with emissions from the individual countries and from international shipping in the Atlantic (ATL) and the North Sea (NOS). Figure 7.5 illustrates the EMEP source–receptor matrices for the UK for the year 2005. These figures can give an indication to policy-makers of limiting factors in the effect of reducing national emissions. For reduced nitrogen, 73% of deposition is attributed to emissions originating from the UK. For oxidised nitrogen and sulphur a significant proportion of deposition (18% and 19% respectively) is attributed to emissions from international shipping in the North Sea and the Atlantic.

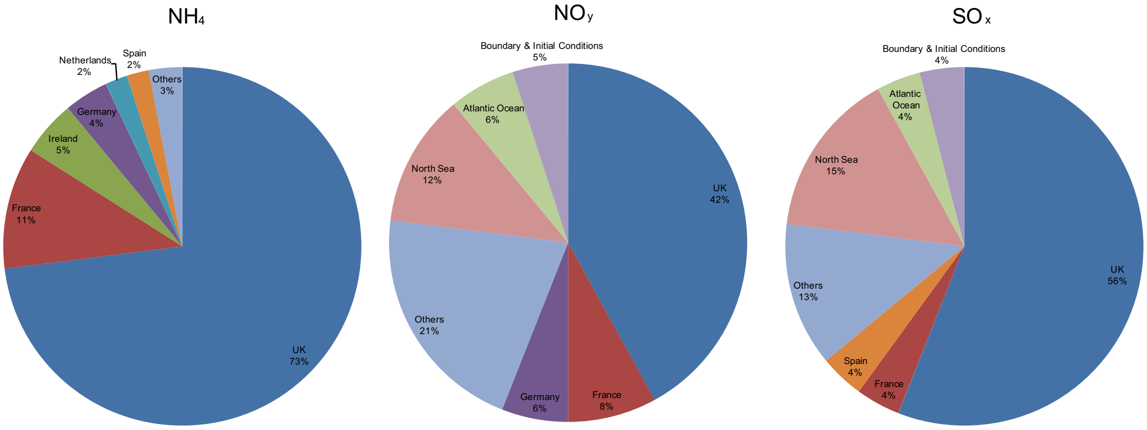

Figure 7.5: Source attribution for deposition in the UK for the year 2005 with the EMEP model for: NH_x deposition (left); NO_y deposition (middle); SO_x deposition (right).

Future development

Sulphur dioxide emissions will continue to decrease over the next 10-15 years due to legislation in place bringing total emissions to approximately 2.9 million tonnes of sulphur dioxide by 2020. In addition, the Thematic Strategy on Air Pollution aims to reduce emissions further; according to calculations by the International Institute for Applied Systems Analysis (IIASA) (July 2008), emissions should, in an optimised scenario, be reduced to approximately 2.3 million tonnes sulphur dioxide (Amann *et al.*, 2008). Maritime emissions are discussed in Section 7.4.

7.2.2 Nitrogen

An illustration of the main pathways of reactive nitrogen compounds in the atmosphere is provided in Figure 7.6. The left side of the figure illustrates the atmospheric pathways of NH_x compounds (gas phase ammonia (NH_3) and aerosol phase (ammonium, NH_4^+)), and the right side of the figure illustrates pathways of NO_y compounds (nitrogen oxides (NO_x) and reaction products). NH_3 is emitted to the atmosphere mainly from agricultural sources. In the atmosphere it is subject to transport and dispersion, but also scavenging by dry deposition and by transformation to aerosol NH_4^+ in reactions with acid gases and aerosols. Aerosol NH_4^+ has a longer lifetime in the atmosphere than gaseous NH_3 and may therefore be transported over long distances (>1000 km). NH_4^+-containing aerosols are mainly removed by wet deposition. Nitrogen oxides (NO_x), are emitted to the atmosphere where they are subject to transport and dispersion. NO_2 may be dry deposited to vegetation, but is mainly scavenged from the atmosphere by reaction with hydroxyl (OH^-) radicals to form nitric acid (HNO_3). HNO_3 has a short lifetime in the atmosphere, since it is quickly scavenged by uptake in aerosols, reaction with NH_3 or dry deposition (it sticks to any surface – aerosol as well as ground). Uptake in aerosols or formation of new aerosols by the reaction with NH_3 leads to aerosol-bound nitrate (NO_3^-). Also NO_3^--containing aerosols (in some cases the same aerosols that contain NH_4^+) are mainly scavenged from the atmosphere by wet deposition. Aerosol phase NH_4^+ and NO_3^- in the atmosphere may under certain circumstances be released back to gas phase NH_3 and HNO_3.

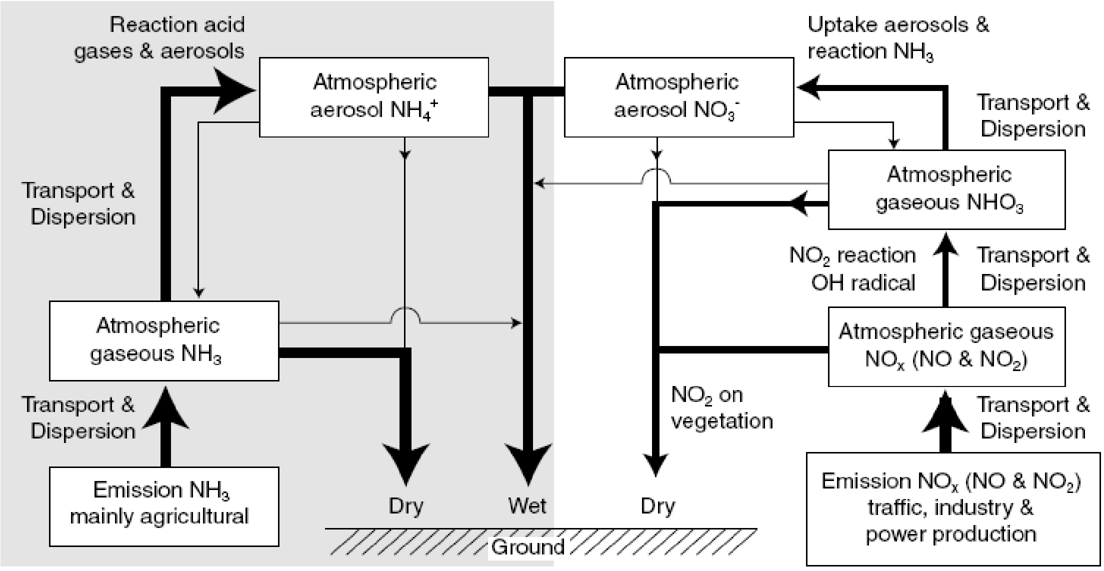

Figure 7.6: Illustration of the main pathways of reactive nitrogen compounds in the atmosphere (Hertel *et al.*, 2006).

On the European scale – more specifically looking at the EU27 domain – emissions of nitrogen oxides have declined from 17.1 million tonnes in 1990 to 11.3 million tonnes in 2005 or by approximately 35% since 1990. With current policies, emissions will continue to decrease and are expected to be approximately 7.7 million tonnes by 2020.

Ammonia emissions have also decreased since 1990, and are projected to decrease further by 2020. Emissions in EU27 were approximately 5.1 million tonnes in 1990 and will, according to baseline scenarios, decrease to 3.1 million tonnes by 2020. Emissions decreased by approximately 20% by 2006; the main decrease occurred in eastern Europe following the political changes around 1990. Considering the entire EMEP domain (including eastern Europe, Russia, Kazakhstan, etc.) the estimated emission reductions are even larger, from 9.2 million tonnes in 1990 to 6.8 million tonnes in 2006 or by 25%. (See also Figure 7.7).

Further reductions are recommended in the proposed revision of the NECD of an additional 0.5 million tonnes for nitrogen oxides, down to 5.2 million tonnes, and an additional 0.6 million tonnes for ammonia, down to 3.1 million tonnes.

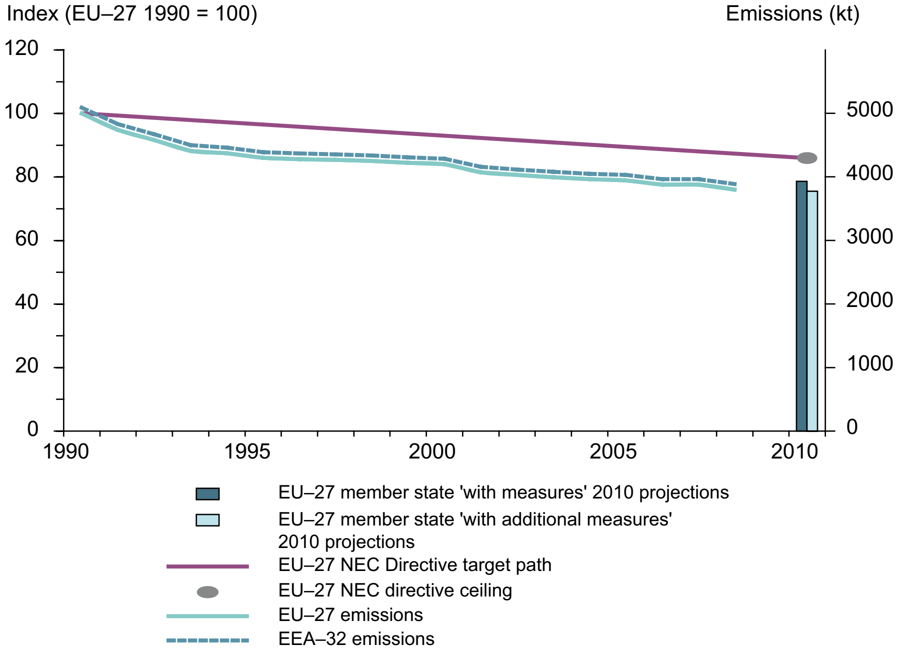

Figure 7.7: Trend in ammonia emissions for EU27 countries for the period 1990 to 2007, and further projected to 2010 (Source EEA).

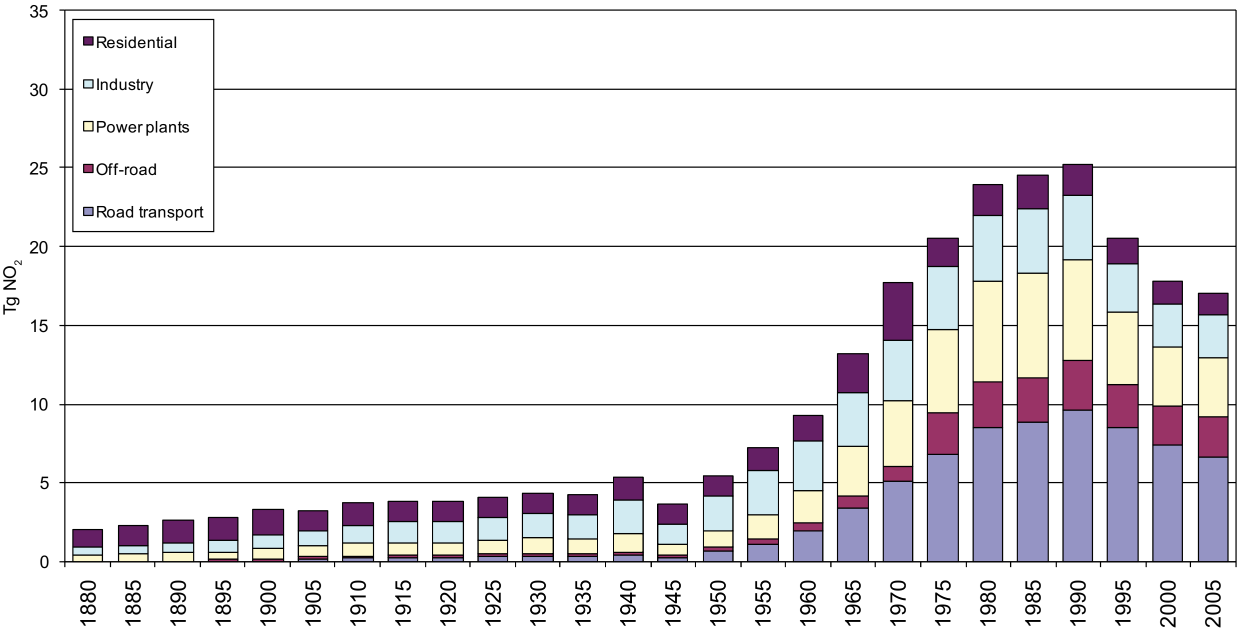

Figure 7.8: Sector trends in European NO_2 emissions 1880-2005 (Tg NO_2) (Vestreng *et al.*, (2009).

Figure 7.8 illustrates the different rates of growth and reductions for the major oxidised nitrogen source sectors in Europe, displaying the significant reductions achieved in particular for road transport and power plants between 1990 and 2005. It is important to note that these emission reductions were achieved while overall energy and transport demand showed marked growth rates throughout this period. For road transport significant reductions were achieved through a series of EU directives over the last 20 years including tail pipe regulations on volatile organic compound (VOC) and NO_x emissions for passenger cars from 1991, which in reality forced the introduction of catalytic converters for gasoline cars. For stationary combustion, the flue gas regulations on large combustion plant (LCP) have played an important role in emission reductions, and have led to both introduction of low NO_x burners and flue gas cleaning (e.g. through the installation of selective catalytic reduction, SCR).

7.3 Ozone

7.3.1 Trends in ozone concentration

Ground level ozone has been recognised as an important pollutant in Europe since the 1970s (Bojkov, 1986; Volz and Kley, 1988) and damaging effects on human health, crops and semi-natural vegetation have been shown to be widespread throughout Europe (NEGTAP, 2001; Royal Society, 2008). The reductions in NO_x and VOC emissions over Europe within UNECE and EU control strategies were in part targeted at control of ground level ozone, as described in Chapter 3. These long-term reductions in ozone precursors were reported in NEGTAP (2001) and accompanied a reduction in peak ground level ozone concentrations of approximately 30% over the period 1980 to 1997. More recent analyses by AQEG (2009) and the European Environment Agency (EEA, 2007) bring these trends up to date and show the changes in ozone concentrations in the UK between 1980 and 2005. The improvements in air quality through reductions in peak concentrations are valuable steps in the process of achieving clean air, however, concentrations large enough to damage human health and vegetation are still common and substantial problems due to ozone throughout Europe remain, especially in warm summers such as 2003. In part the problems require further reductions of the ozone precursor gases within Europe, but recent analyses of the ground level ozone problem show the issues to require emission reductions on a much larger geographical scale (i.e. hemispheric) to be fully effective in protecting human health and ecosystems in Europe. In this section the analyses provided by the Royal Society (2008) and AQEG (2009), and recent academic literature are briefly summarised to show the nature of the issue of ground level ozone in Europe, the effect of emission reductions in Europe to date, and the likely interactions with climate change in the coming decades.

The trends in ground level ozone over the last two decades have been reported for a range of European sites. At high altitude sites in the Alps, annual mean surface concentrations have increased at a rate of about 0.4 ppb per year with the smallest increase during the summer months (0.19 ppb per year) and the largest increase during the winter months (0.53 ppb per year), as shown in Figure 7.9 from the work of Staehelin and Poberaj (2008).

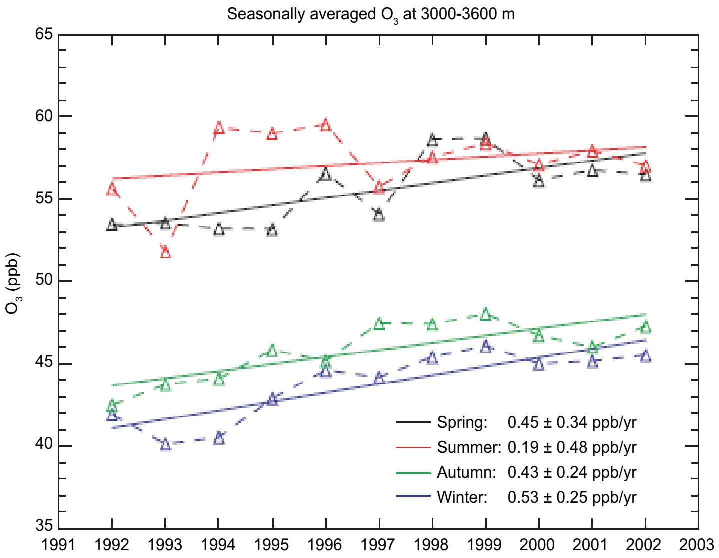

Figure 7.9: Trends in seasonal ground level ozone on three European mountains (Jungfraujoch, Zugspitz and Sonnblick) over the period 1992 to 2002 (Ordóñez, 2006).

The long-term trends are clearly evident at high altitude locations in central Europe, remote from the local influences of urban emissions, which also show an increase in ozone concentrations due to reductions in the local depletion of ozone by nitric oxide. The absolute values for the annual mean ozone levels in the range 40-55 ppb are sufficiently large to represent a threat to human health and vegetation, so clearly policy development needs to address not just the peak values, but the background.

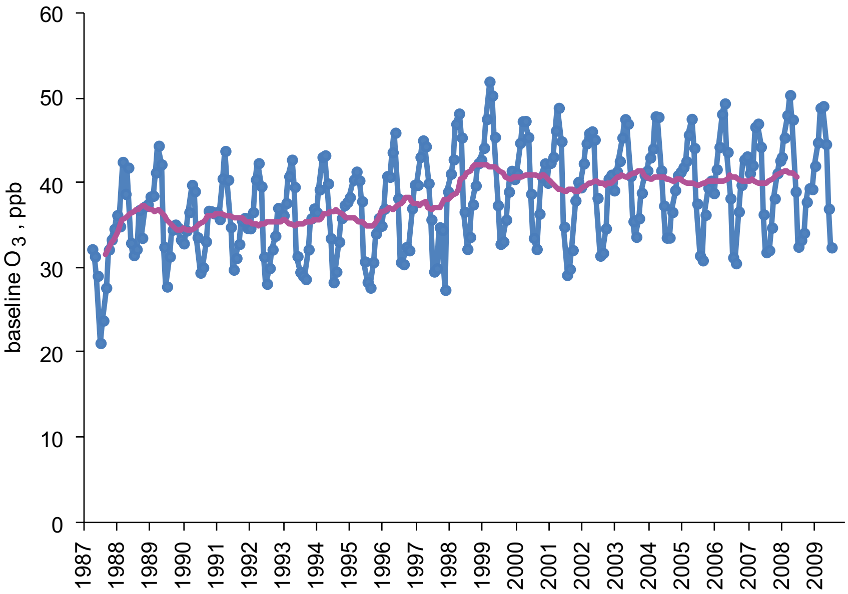

Figure 7.10: Trends in monthly mean baseline ozone levels at Mace Head on the west coast of Ireland between 1986 and 2006, including a running 12-month mean (pink line), showing the ~5 ppb increase in ozone mixing ratios over 20 years.

The upward trend in ground level ozone is also evident at sites in the UK and Ireland. At the west coast site at Mace Head in Ireland, the monthly mean baseline ozone levels have increased by approximately 5 ppb (~0.2 ppb yr^{1}) over the last 25 years, as shown in Figure 7.10.

These changes in mean levels conceal important changes in the frequency distribution; peak values have declined steadily over the last 20 years as a consequence of emission reductions in Europe, whilst the lowest percentiles have increased as a consequence of emissions throughout the northern hemisphere (Royal Society, 2008). The changes in the frequency distribution of ground level ozone concentrations are illustrated for two UK sites in Figure 7.11 – an urban site close to the centre of Leeds in northern England and a rural site in Southern England, close to the south coast (Lullington Heath). The data for these sites show over the last 20 years a trend of decreasing peak values and increasing median and lower percentile concentrations (Jenkin, 2008). The trends shown are typical of many similar sites in the UK and more widely in northern Europe.

The main cause of growing background ozone levels is the growth in northern hemispheric ozone precursors over the last 20 years, including rapidly growing emissions from the expanding economies of south-east Asia and from international shipping (discussed later in this chapter).

The consequence of these trends is that the benefits of reductions in European emissions have been significantly eroded by the growing hemispheric ozone levels from emissions outside Europe. An important policy consequence of this trend is that policy to provide effective control of ozone in Europe requires emission control on the main precursors at a much larger geographical scale, preferably hemispheric, and importantly must include international shipping and aviation (Royal Society, 2008).

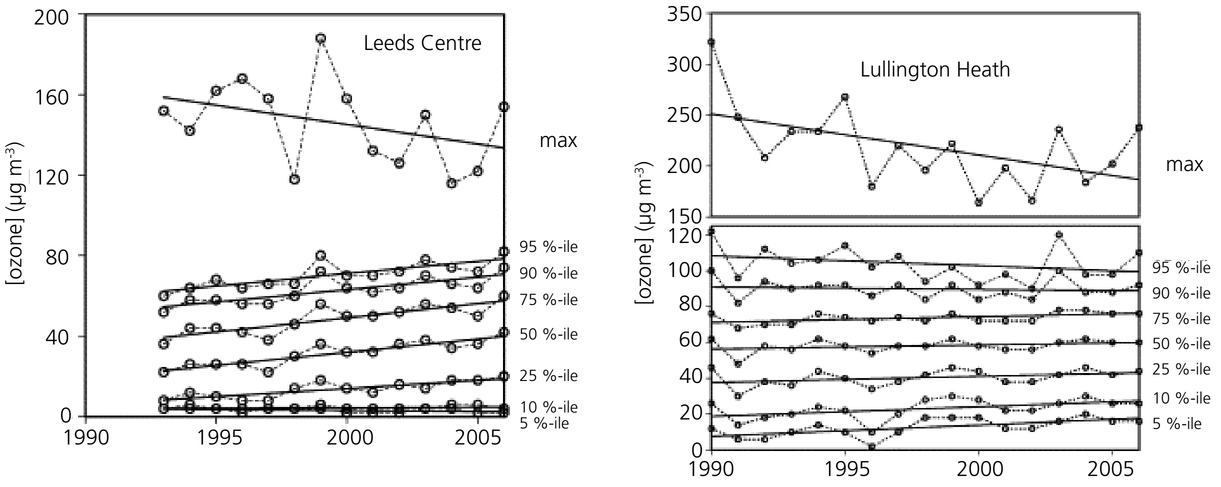

Figure 7.11: Changes on ground level ozone at an urban city centre (Leeds) and a rural location (Lullington Heath) in the UK (from the work of Jenkin (2008)).

7.3.2 Evidence of impacts of ozone in Europe

Over the past two decades, a significant body of work has been conducted in different regions of Europe to assess the impacts of ozone on vegetation in the field. The field evidence of effects on crops and semi-natural vegetation has recently been compiled (Hayes *et al.*, 2007b; Mills *et al.*, 2011). This synthesis of the evidence in the field, based on visible symptoms of ozone injury, effects on growth in a clover biomonitoring system and experiments in which ambient air has been filtered to remove ozone, provides a strong basis for establishing the significance of ozone as a pollutant across the continent. For example, Hayes *et al.* (2007b) identified 644 separate records of visible injury, for a total of 27 crop species and 77 species of semi-natural vegetation over the period 1990-2006 (see Figure 7.12).

The intensity of the recording effort collated by Hayes *et al.* (2007b) varies across Europe, and hence precise quantification of the geographical distribution of ozone damage to vegetation is not possible. However, the extent of the database does allow three important conclusions to be drawn:

1. The frequency of visible injury was greatest in continental central Europe and the western Mediterranean, which accounted for 75% of the observations of confirmed injury. The effect of ozone in reducing growth in the clover clone biomonitoring system was also greatest in these two regions.
2. The frequency of visible injury and the extent of growth reduction in the clover clone biomonitoring system was lower in Atlantic central Europe, which includes the UK. Although ozone effects were less significant here than in the centre of Europe, they are part of a continuum of effects across almost the whole continent.
3. The geographical range of the modelled exceedance of the critical level for ozone based on the AOT40 exposure index, which shows maximum exceedance in southern Europe, did not account for the observations of adverse effects of ozone in central and northern Europe. There was a much greater consistency between the extent of the area of observed effects of ozone and modelled ozone flux, especially when a clover-specific flux model was used. This provides further support for the use of a flux-based index in place of AOT40 for ozone risk assessment, as discussed in Chapter 5 of this report.

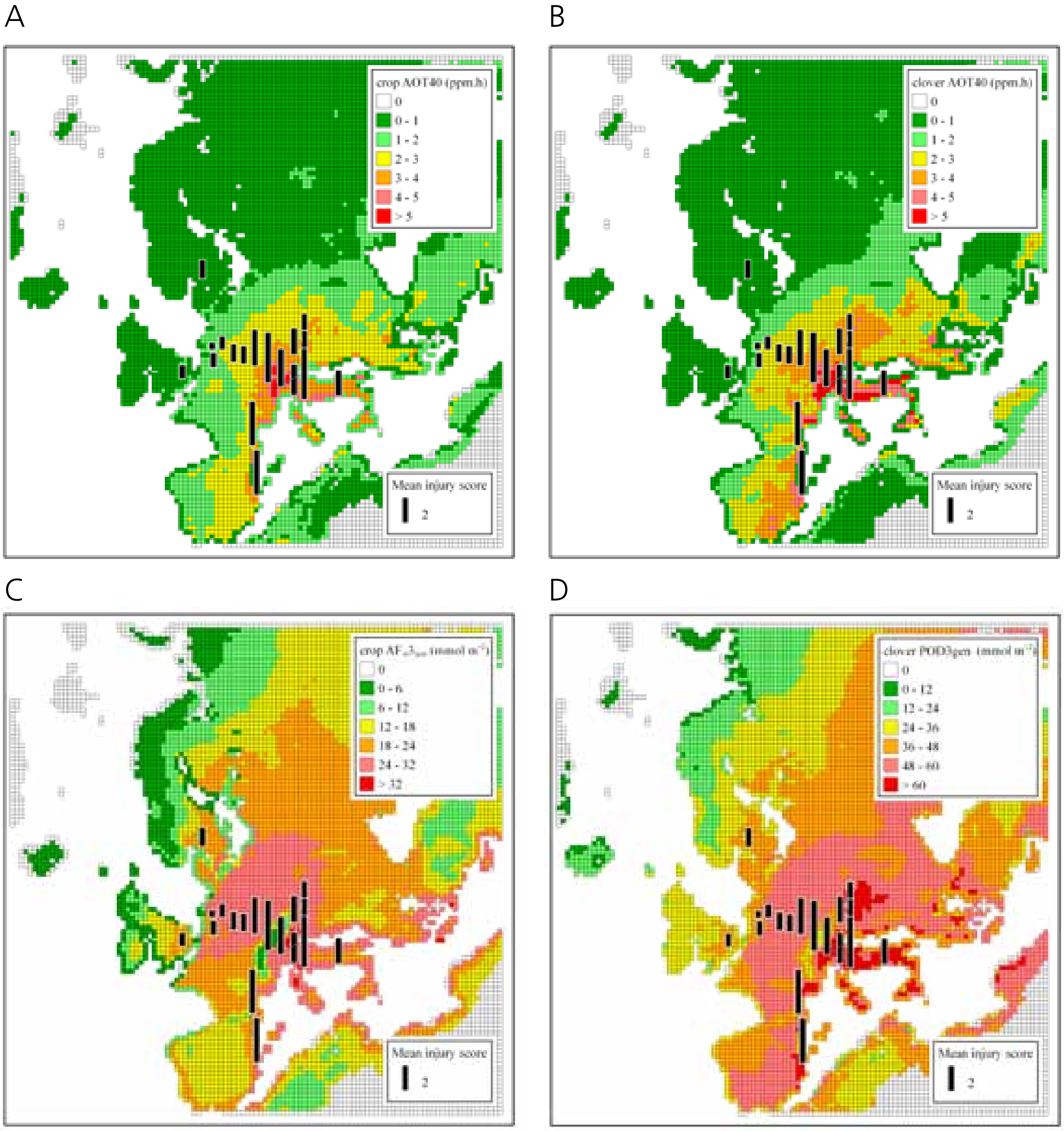

Figure 7.12: Five-year mean ozone injury score (June to August) on ozone-sensitive white clover (NC-S) at ICP Vegetation sites for the period 2000-04 superimposed on the EMEP five-year mean for (a) AOT40 (crop), ppm.h; (b) AOT40 (clover), ppm.h; (c) POD3$_{gen}$ (crop), mmol m^{-2}; and (d) POD3$_{gen}$ (clover), mmol m^{-2} for the same years (Mills *et al.*, 2011).

7.4 Shipping

Emissions from shipping are becoming increasingly important for European air quality, in particular for the deposition of oxidised sulphur and nitrogen compounds and for ground level ozone. The world seaborne trade increased at typically 3-6% per year between 1987 and 2007 and annual tonne-miles travelled have more than doubled over this period. An estimate of fuel consumption indicates that annual consumption increased by a factor of 4.3 between 1950 and 2001 (Eyring *et al.*, 2005; Fearnleys, 2007). Although there are some deviations in emission estimates, it is obvious that shipping is a sector with a large growth in emissions over the last decades.

Scenarios of emissions from shipping indicate that there will be an ongoing increase in demand for sea transport and that fuel consumption may increase substantially until 2020. In an IIASA scenario from 2007, emissions are estimated to increase by 50% between 2000 and 2020 (Cofala *et al.*, 2007). Since then, the International Maritime Organization (IMO) has agreed to reduce the sulphur content of fuel continuously over this period to a maximum sulphur content of 0.5% from 2020. In so-called 'Emission Control Areas' there will be stricter control with a maximum sulphur content in fuel of 0.1% by 2015. Nitrogen oxides were also included in the IMO agreement but the controls requested were much weaker and emissions will, according to scenarios, continue to increase. Due to the crisis in the financial market and the expected depression in the world economy, freight requests are expected to decrease. International shipping is very sensitive to economic conditions and emissions from shipping are therefore difficult to forecast.

7.4.1 The influence of shipping on European air quality and policy

The influence of shipping on European air pollution was thoroughly investigated in the context of the revision of the NECD (Cofala *et al.*, 2007). The study indicated that international shipping typically contributed 10-20% of the total sulphur deposition in coastal areas in 2000. In the baseline scenario (without the IMO-agreed control of sulphur emissions), the relative contribution to sulphur deposition will increase to typically 20-40% by 2020 (Figure 7.13). The level of control of sulphur emissions will probably maintain the relative contribution from shipping in 2020 at the same level as it was in the year 2000.

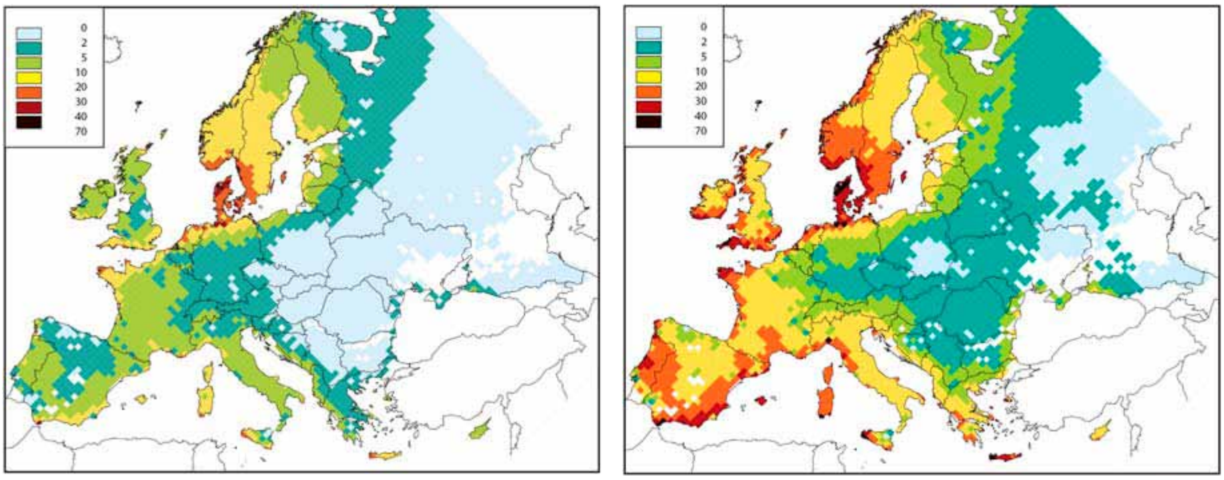

Figure 7.13: Percent of sulphur deposition originating from international shipping in (a) in 2000 and (b) for the 'Baseline' scenario in 2020 (Values calculated with average transfer coefficients for five meteorological years (1996, 1997, 1998, 2000 and 2003).) (Cofala *et al.,* 2007).

Shipping also contributes to nitrogen deposition and ground level ozone production. The IMO agreement on NO_x emissions will decrease emissions per tonne transported, but since overall transport is expected to increase, one may at the best expect *status quo* in NO_x emissions.

7.5 Environmental achievements and ways forward

Since the NEGTAP (2001) report, interest in studying the signals of recovery from air pollution effects, as observed through scientific projects and established monitoring networks, has grown, in particular under the Convention on Long-range Transboundary Air Pollution (CLRTAP). Changes in the impact on UK ecosystems in response to reductions in emissions of atmospheric pollutants are reviewed in Chapter 8, Recovery.

7.5.1 Sulphur and acidification

The decrease in sulphur deposition has reduced areas of critical loads exceedance over large parts of Europe, in particular for freshwater acidification. The problem of freshwater acidification is today, to a large extent limited to the Nordic countries and some parts of the UK. The reason is that these areas have a majority of the lakes in Europe within catchments of slowly weathering bedrock and therefore soils with limited acid neutralising capacity (ANC). For soil acidification, large parts of Europe still experience deposition in excess of critical loads (Figure 7.14). The problem of soil acidification is to a large extent a problem for the European continent north of the Alps, UK and the most southern parts of Scandinavia. Large parts of Europe will meet critical loads by 2020, in particular the inland areas of the continent. According to the scenarios, improvements will be large for UK and large parts of Scandinavia. Areas, which will still show substantial exceedances are Benelux, parts of northern France and south-west Norway.

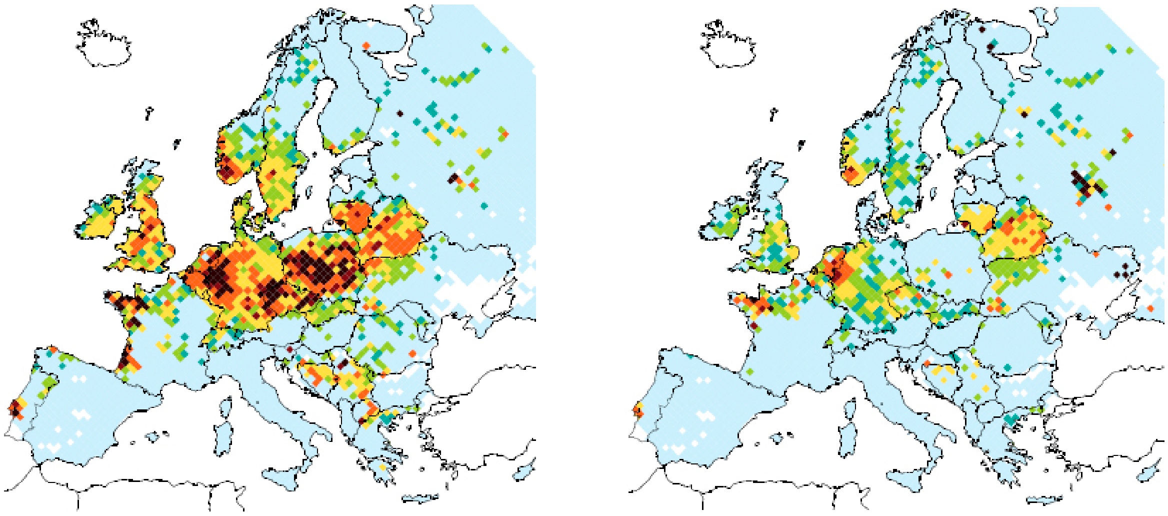

Figure 7.14: Percentage of forest area where acid deposition exceeds the critical loads for acidification (a) in the year 2000 and (b) for the optimised scenarios in 2020 (Amann *et al.*, 2008).

For acidification, there have been strong chemical responses with respect to sulphate concentrations and ANC as well as pH in surface waters over practically all of Europe (Skjelkvåle and De Wit, 2008). Trend analysis indicates a faster decrease in terms of sulphate concentrations during the 1990s than periods before Figure 7.15. There are also widespread signs of recovery, but the recovery has not yet reached levels where widespread recolonisation and development of pre-industrial situations can be detected. Due to the slow recovery, there has been an increasing interest in studying the recovery processes through theoretical models. Through these models, a better understanding has been achieved of the processes determining chemical recovery and the interplay between atmospheric deposition, soil and vegetation processes and finally the responses in lakes. Scenario studies with simulation models show that even if recovery processes start when deposition is below critical loads, recovery is a process that will in many areas go on for many decades.

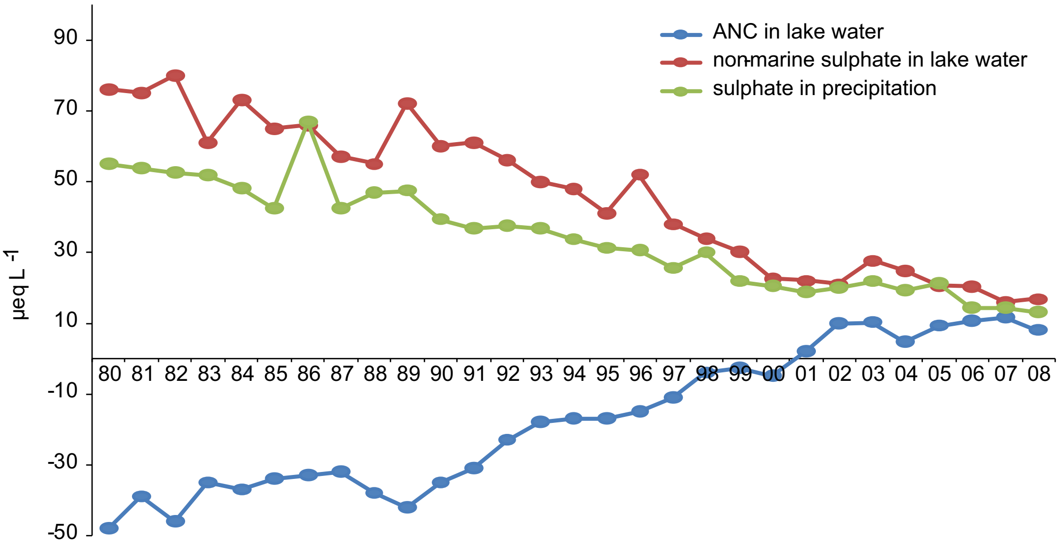

Figure 7.15: Annual mean concentrations of 'non-marine' sulphate in precipitation and lake water, and acid neutralising capacity (ANC) at ICP Waters site NO10 (Storgama) in southern Norway, from 1980 to 2006 ('Non-marine' sulphate is calculated by removing trace amounts of sulphate originating from sea-salt spray from total sulphate concentrations in precipitation. The figure shows that sulphate concentrations in lake water respond to reductions in sulphate in precipitation, and that lake acidity responds to reduced sulphate in the lake water.) (Skjelkvåle and De Wit, 2008).

7.5.2 Nitrogen

Nitrogen (N) deposition from the atmosphere is an important contribution to transboundary pollution issues because through this pathway N can reach and enrich sensitive ecosystems far away from the sources of emission. However, deposition is only part of the whole nitrogen cycle; and one molecule of nitrogen, once deposited, can cascade through the environment, changing form and contributing to several effects (Galloway *et al.*, 2003). The global nitrogen cycle has been extensively perturbed by human activities such that two thirds of the fixed nitrogen cycling through the atmosphere and back to the Earth's surface is anthropogenic in origin (Galloway *et al.*, 2003) Atmospheric transport is an important part of the nitrogen cycle, but water transport is also relevant. Progress has been made in reducing NO_x emissions in the UK and Europe. As a result of the stronger decrease in SO_2 emissions, atmospheric particle chemistry has changed, favouring more ammonium nitrate formation and leading to a gradual change in the transport distances for reactive nitrogen with time. Therefore, the decrease in deposition in remote areas is smaller than the decrease in emissions. Fertiliser production and use has varied with time, increasing during the period 1950 to 2006.

Ammonia is an important pollutant contributing to a range of effects on ecosystems and the atmosphere, and stronger reduction targets are needed in the future. Furthermore, measures to reduce ammonia have been shown to increase leaching of nitrogen to freshwaters (pollutant swapping). Reduction in reactive nitrogen production is essential to decrease eutrophication and acidification effects, but also to decrease the cascade of effects.

Effective nitrogen management measures should focus on reducing the creation of reactive nitrogen, increasing its efficiency of use, reuse of nitrogen and conversion into nitrogen gas (N_2). One way of directing nitrogen management is to use nitrogen budgets at different scales or in different sectors and find ways to lower the excess.

7.5.3 Impacts of scale/resolution of deposition models on UK critical load exceedances

Terrestrial impacts of pollutants in Europe have been assessed using critical loads methods. The assessment over Europe, primarily using the EMEP model to provide pollutant deposition has been at a grid resolution of 50km x 50km. The grid scale of the modelling and assessment influences the exceedance, (e.g. Lövblad *et al.*, (1995)). In general, all studies to date show that decreasing the scale leads to larger exceedances of critical loads in the most sensitive grids and thus a larger demand for control to meet air pollution policy targets.

For the UK, critical load exceedances have been mapped using two different methods of estimating atmospheric deposition: (i) using EMEP data which generate deposition estimates for 50 km x 50 km grid squares; and (ii) using measured deposition data based on national-scale CBED data assuming constant deposition within each 5 km x 5 km grid square. Exceedances were estimated for a number of sensitive Broad Habitats (nine habitats for acidity, ten habitats for nutrient nitrogen). Critical loads are mapped for these habitats on a 1 km x 1 km grid scale. In calculating exceedances, ecosystem-specific values of deposition were applied as follows: (a) values for moorland/semi-natural vegetation applied to non-woodland terrestrial habitats; (b) values for woodland/forest applied to woodland habitats; and (c) average values for all habitats applied to freshwater habitats represented by their catchment areas.

The areas of Broad Habitats in exceedance of critical loads have been compared using CBED 2004-06 and EMEP 2006 deposition data. The results are summarised in Table 7.2.

Table 7.2: Comparison of critical load exceedances using CBED (2006-08) and EMEP (2006) deposition data. Source CEH/RoTAP.

Country	Percentage area of Broad Habitats exceeded for:			
	Acidity		Nutrient nitrogen	
	CBED	EMEP	CBED	EMEP
England	68%	46%	86%	52%
Wales	80%	44%	87%	32%
Scotland	43%	8%	39%	8%
Northern Ireland	70%	35%	83%	29%
UK	54%	22%	58%	23%

Differences in spatial resolution and patterns of deposition from CBED and EMEP lead to substantial differences in estimates of the area where critical loads are exceeded, with EMEP deposition data suggesting smaller exceedances than those calculated using the higher resolution CBED data. Such differences are likely to occur with models/methods designed for different spatial scales and application. It is therefore important to note from a policy perspective that reports presenting European-scale results (e.g. CCE Status Reports, UNECE documents, etc.) are usually based on EMEP deposition data, and will therefore show lower areas of exceedance for the UK, as well as for many other countries, than shown in national reports based on national-scale deposition data/models. This will in general lead to an overestimation of the area protected through European policies. Whether a more detailed estimate of atmospheric deposition on a European scale will also lead to significant differences in priority setting is less certain.

7.6 Effects of climate change on transboundary air pollution

7.6.1 Climate change – Air pollution feedback mechanisms

Distributions and concentrations of air pollutants are perhaps most obviously affected by the magnitude and location of anthropogenic emissions. However, the physical state of the atmosphere and the Earth's surface can also strongly influence air quality, by affecting emissions, transport, mixing, transformation and deposition processes. These effects are most evident in short-term fluctuations in air quality associated with changes in weather conditions. More subtle, longer-term changes in air quality may be occurring due to climate change, and these may become more significant in the future as climate change is expected to accelerate. Many of these process changes directly or indirectly affect the composition of the atmosphere both through the emission, transport, transformation and removal terms in the continuity equations for the atmospheric constituents:

- Transport terms are controlled by advection, convection and mixing properties in the atmospheric boundary layer, including the evolution of the depth of the mixed layer and the entrainment of free tropospheric air. The frequency and intensity of frontal passages are important factors.

- Transformation terms are controlled by relative humidity, specific humidity, cloud cover and type, temperature, albedo and its effect on photolysis rates.
- Removal terms are controlled by precipitation frequency and amount, surface properties like vegetation composition and state, the partial pressures of oxidised and reduced nitrogen in terrestrial surfaces, and relative humidity.
- Emission terms combine both anthropogenic sources, which are determined by the level of economic activity and its geographical distribution, and the extent to which measures are taken to control emissions.
- Changes in temperature, energy consumption, plant and forest species, and atmosphere–ocean interaction are important for the magnitude of biogenic emissions. Drought conditions and the amount of stored carbon in terrestrial ecosystems are important factors in how forest and biomass fires impact on the composition of the atmosphere. If there are changes in the occurrence of extended dry periods, together with high wind incidents, the atmospheric source of dust will increase.

7.6.2 Climate change impact on air pollution

Transboundary air pollution is interpreted as the contribution of one country to the deposition or ambient air concentration in another. Inadvertent changes in transboundary transport as a consequence of climate change can arise from changes in any of the parameters listed above. In addition, measures taken to mitigate climate change can impact on transboundary fluxes of air pollutants, including fuel switching from fossil fuels to biofuels, or reduction of methane emissions by changing the practices of waste handling, agriculture and natural gas distribution. The European Environment Agency recently concluded that climate change policies can make a substantial contribution to reducing air pollution (EEA, 2006).

Many chemical reactions proceed more quickly at higher temperatures, and some key reactions have a strong temperature dependence. Ozone production depends on NO_2 concentrations. A fraction of NO_2 is sequestered in the reservoir species PAN (peroxyacetyl nitrate) through the reaction:

$$NO_2 + CH_3COO_2 \rightarrow PAN \qquad (R1)$$

PAN is subject to thermal decomposition, essentially the reverse of the above reaction:

$$PAN + M \rightarrow NO_2 + CH_3COO_2 \qquad (R2)$$

Reaction R2 is strongly temperature-dependent, so as temperature increases, PAN is less stable, and more of the oxidised nitrogen is present as NO_2. This means that as the climate warms, for the same magnitude of NO_x emission, the NO_2 concentration will be higher in the source region, but lower in more distant regions. The net impact on O_3 concentrations will depend on the local NO_x regime at a particular site.

Higher temperatures increase evaporative anthropogenic volatile organic compound (VOC) emissions (e.g. Rubin *et al.,* (2006), and also enhance biogenic VOC emissions (e.g. Guenther *et al.,* (1995; 2006). Ozone is enhanced by higher VOC levels.

Boundary layer depth exerts a strong influence on ground level pollutant concentrations, as it determines the volume of air that surface emissions are diluted into, and also the volume of air that is subject to dry deposition processes. These effects are clearly evident in the diurnal cycles of many pollutants. Boundary layer stability, and the rate of exchange of air between the boundary layer and the free troposphere determine vertical mixing and dilution; wind speed determines the horizontal dispersion of pollutants. Some emissions, such as dust and sea-salt aerosol, increase as wind speeds rise.

Changes in large-scale circulation can also influence air quality by changing the routes or transit times of background pollutants subject to long-range transport, such as the trans-Atlantic transport of ozone, aerosols and their precursors (e.g. Hess and Lamarque, (2007). Jacob and Winner (2009) conclude that "the future climate is expected to be more stagnant, due to a weaker global circulation and a decreasing frequency of mid-latitude cyclones".

The observed correlation between surface ozone and temperature in polluted regions points to a detrimental effect of warming. Coupled general circulation model-chemical transport model (GCM–CTM) studies show that climate change alone will increase summertime surface ozone in polluted regions by 1–10 ppb over the coming decades, with the largest effects in urban areas and during pollution episodes. This climate penalty means that stronger emission controls will be needed to meet a given air quality standard. Higher water vapour levels in the future climate are expected to decrease hemispheric ozone levels, so that pollution and background ozone have opposite sensitivities to climate change. Increases in the stratospheric source of ozone, due to both an intensified Brewer–Dobson circulation (Butchart *et al.*, 2006) and recovery of stratospheric ozone (Eyring *et al.*, 2007) are likely in future. Such changes are likely to influence hemispheric ozone levels.

The effect of climate change on particulate matter (PM) is more complicated and uncertain than for ozone. Precipitation frequency and mixing depth are important driving factors but projections for these variables are often unreliable. GCM–CTM studies find that climate change will affect PM concentrations in polluted environments by ±0.1-1 $\mu g\ m^{-3}$ over the coming decades. Wildfires fuelled by climate change could become an increasingly important PM source.

These conclusions are drawn on the basis of time correlations of observations of air pollution trends and temperature trends, and on the present capability of chemical transport models (CTMs), or coupled general circulation models and CTMs (GCM-CTM), to capture the main processes controlling the air pollution load.

Changes in the hydrological cycle may also influence air quality. A warmer atmosphere holds more water vapour. Over most of the atmosphere, at sites remote from anthropogenic emissions, NO_x levels are sufficiently low that increased levels of water vapour enhance net ozone destruction. However, in polluted regions, where NO_x levels are relatively high, more water vapour leads to increased net ozone production (Isaksen *et al.*, 2005). Photochemical oxidants, such as ozone and the hydroxyl radical (OH^-), are influenced by levels of ultraviolet (UV) radiation, which are strongly modulated by clouds. Biogenic VOC emissions increase with PAR (photosynthetically available radiation) (Guenther *et al.*, 2006). Convective clouds cause rapid and vigorous vertical mixing (Doherty *et al.*, 2005), and lightning, which generates NO_x (Schumann and Huntrieser, 2007). Cloud droplets provide the substrate for aqueous phase chemistry, the dominant route for the oxidation of SO_2 to sulphate. Many hydrophilic pollutants (e.g. most aerosols, nitric acid, hydrogen peroxide, etc.) are subject to wet scavenging, so will be influenced by changes in precipitation. Soil moisture is an important determinant of stomatal conductance, and uptake of pollutants such as ozone by vegetation is often the dominant removal pathway in the boundary layer.

7.6.3 Summary

As judged from the scientific literature in general and reflected in the Jacob and Winner (2009) review, the current capability to characterise air pollution–climate change feedbacks is quite immature. In many cases, the changing climate induces significant changes in air pollution controlling parameters over a very broad range of processes, and over a broad range of spatial and temporal scales, and many of these changes introduce feedbacks that compensate each other. The variability in the observed fields of individual pollutants is large, as is the case for the many processes controlling them, indicating that a large number of measurements are needed to identify significant correlations.

Changes in transboundary transport of pollution as a consequence of climate change appear from current knowledge to be second order effects relative to the climate change impact on air pollution concentrations, and it is probably premature at this stage to generalise further.

Two case studies identifying positive feedbacks between climate change and air pollution

There are a few specific studies, such as that by Langner *et al*. (2005), in which simulations with the European-scale chemical transport model MATCH indicate substantial potential impact of regional climate change on both deposition of oxidised nitrogen and concentrations of surface ozone in Europe. These calculations were 'time slices' corresponding to present climate while the scenario time slices corresponded to a future situation with a global mean warming of 2.6K realised in the period 2050–2070 depending on the GCM used to derive the meteorological driver data. The simulations showed a strong increase in surface ozone concentrations over southern and central Europe, and a decrease in northern Europe. Changes in deposition of oxidised nitrogen were much smaller and also varied depending on the GCM used for meteorological driver data. Langner *et al*. (2005) found that the changes in simulated annual deposition were significant only in relation to interannual variability.

In a case study of the pollution loads in the boundary layer over Europe in the summer 2003 heatwave, Solberg *et al.* (2008) found that the 99th percentile of daily maximum ozone in 2003 was higher than the corresponding parameter measured in any previous year at many sites in France, Germany, Switzerland and Austria. The concentrations were particularly high in June and August 2003. Positive feedback effects between the weather conditions and ozone contributed to the elevated surface ozone. An extended residence time of air parcels in the atmospheric boundary layer was calculated. It was likely that extensive forest fires on the Iberian Peninsula, resulting from the drought and heat, contributed to the peak ozone values in northern Europe in August. Measured isoprene concentrations were approximately twice as high in summer 2003 as in previous years, either reflecting increased biogenic emissions, reduced atmospheric mixing or a combination of the two. Biogenic isoprene could have contributed about 20% of the peak ozone concentrations. In a CTM sensitivity calculation it was shown that a reduction in surface dry deposition due to drought and elevated air temperature could have contributed significantly to enhanced ozone concentrations, through both reduced loss to the surface by dry deposition and more efficient photochemical formation. Solberg *et al.* (2008) speculated that due to climate change, episodes like the summer 2003 heatwave in Europe may occur at a higher frequency in the future and may gradually overshadow the effect of reducing emissions from anthropogenic sources of VOC and NO_x.

It is currently uncertain what the contribution of climate change to date has been towards UK air quality trends. Hulme *et al.* (2002) report that future climate change is expected to increase temperatures over the UK, with a rise in the numbers of heatwaves. Winters are likely to be wetter, whilst summers are likely to be drier, although the UK is close to the latitude where precipitation trends change from being generally drier (southern Europe) to being predominantly wetter (northern Europe) (e.g. Christensen *et al.* (2007)), so future trends in precipitation are relatively uncertain. High resolution model projections of the net impacts of these potential future changes in climate on UK air quality do not currently exist.

7.6.4 Intercontinental transport and emissions imported from outside Europe

With the dominating westerly air flows over Europe, emissions from the North Atlantic and North America directly influence air pollution in Europe, in particular the western parts of the continent. This influence will, for some coastal areas, be of such a magnitude that it will significantly increase target exposures (e.g. ozone exposure to vegetation). The magnitude of intercontinental transport is being estimated through the UNECE Task Force on Hemispheric Transport of Air Pollution; the first set of data was presented in 2007 (UNECE, 2007).

The photochemical oxidant and tropospheric ozone problem in North America appeared somewhat earlier than in Europe and more stringent control on cars occurred in California during the late 1970s. Stringent controls on motor vehicles were introduced in Europe about 10 years later. For acid deposition the situation was to some extent the opposite. Emission control started earlier in Europe than in the US. Even with a more stringent control of NO_x emissions in the US, legislation was only able to keep emissions constant until the late 1990s. During the last 10 years US NO_x emissions have started to decrease significantly. For sulphur dioxide there has been a more steady reduction in emissions; emissions in 2006 are approximately 50% of the emissions reported in 1980.

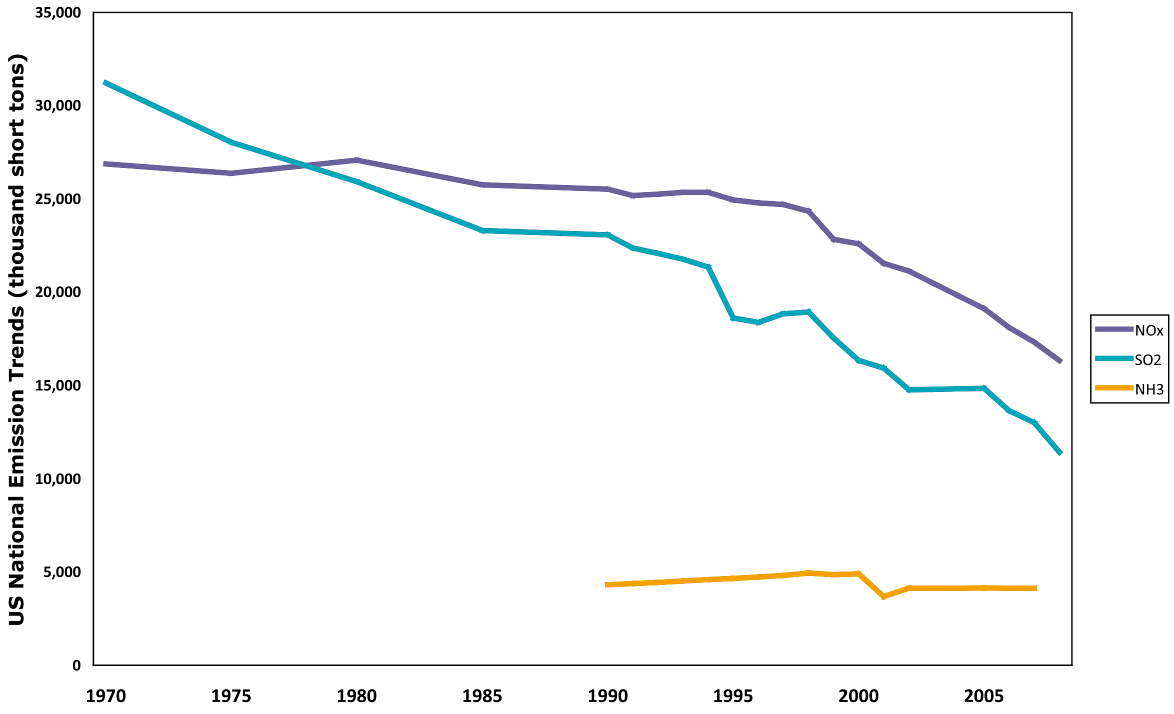

Figure 7.16: US emission trends for nitrogen oxides, sulphur dioxide and ammonia 1980-2007 (EPA, 2009).

Emissions have so far been reduced at a much lower rate in the US than in Europe. This is particularly the case for sulphur dioxide, where European achievements are much larger than those in the US (Table 7.3).

Table 7.3: Emissions of sulphur dioxide, nitrogen oxides, ammonia and VOCs in the US and EU27 for the period 1990 and 2005 (Data from US EPA and EEA).

Compound	US 1990	US 2006	Trend %	EU27 1990	EU27 2006	Trend %
SO_2	23077	14714	-36	27323	8284	-70
NO_x	25527	17694	-23	17136	11294	-34
NH_3	4320	4135	-4	5120	4094	-20
VOC	24108	19976	-17			

7.6.5 Task Force on Hemispheric Transport of Air Pollutants (TFHTAP)

In 2004 the US and the EU took the initiative to form a Task Force under CLRTAP with the aim of quantifying and assessing the importance of intercontinental transport of air pollution. The Task Force has formed a strong scientific basis with participation not only from CLRTAP signatories but also from countries representing south and east Asia. The Task Force has included in its work intercontinental transport of ozone and its precursors, aerosols and mercury. Priority so far has been given to an assessment of the evidence for transport, the establishment of coherent emission inventories and emission scenarios, an intercomparison of atmospheric transport and chemistry models operating on a hemispheric scale, and on the compilation of monitored data for verification of models. The first report focusing on intercontinental transport of ozone and its precursors, and aerosols was published in connection with the review of the Gothenburg Protocol (UNECE, 2007). A full assessment report of the work within the Task Force will be presented in 2010. So far, the work has focused on industrial emissions rather than emissions from shipping and aircraft.

7.7 The future: Is Europe on its way towards becoming a clean air continent?

European air pollution control has achieved considerable success. Emissions have been reduced and current policies will reduce air pollution further by 2020. The future after 2020 is uncertain in terms of future regulations on air pollution but it is expected that emissions will continue to decrease over the European continent due to several reasons:

- Air pollution effects on human health. Air pollution policies recently agreed in the European Commission will improve air quality but there is still a strong signal from air pollution in effects on human health. If the future health-driven policy is directed at fine particles in general, there will be strong pressure to further reduce S and N emissions.
- Strong synergies between air pollution and climate change policies. Climate change policies will lead to energy conservation and changes in fuel types, both leading to a decrease in emissions of sulphur dioxide and nitrogen oxides. In the longer term, ‘carbon capture and storage’ (CCS) may lead to further decrease in emissions.
- Emission controls in the maritime sector. Agreements within the International Maritime Organization (IMO) in October 2008 to limit the sulphur content of fuel oil to 0.5% by 2020 will reduce emissions of SO_2. However, IMO have so far failed to agree an emission reduction on nitrogen oxides.

European air pollution policies have depended on scientific research, monitoring and science-based models using a concept based on critical loads and levels, source–receptor relationships and cost-effectiveness. The methodology has been successful and formed the basis for the Oslo and Gothenburg Protocols under CLRTAP, and the EU NECD. It also formed the basis for the Thematic Strategy for Air Pollution (the CAFE work) prepared by the European Commission (CEC, 2005).

Will this methodology be useful in the future? The answer is probably both yes and no. The original concept has already been revised and there are changes in the ways critical loads and levels are defined, calculated and used. As shown in this chapter, the concepts are to a large extent dependent on definitions and how results from models and inventories are integrated at regional scales.

During the 30 years CLRTAP has been in operation, European air pollution strategies have considered air pollution problems in isolation from external factors such as land use, forest management practices and climate change. In the future, it is clear that these factors need to be considered and future strategies need to take into account, for example, changes in agricultural policies and increased demand for biofuels. To integrate the effects of climate change into air quality control measures it will be necessary to include changes with respect to control options and costs and also the influence from a changing climate on the emissions, behaviour and effects of atmospheric pollutants.

From an acidification/eutrophication perspective, efforts need to be concentrated on two emission source categories to meet long-term objectives in terms of protecting European ecosystems:

- Ammonia emissions: European emissions are, according to present policy, expected to decrease by at most 10% in 2020 compared to emissions in 2000 (Amann *et al.*, 2008). Thus, as other emissions continue to decline, the relative importance of ammonia will increase.
- NO_x emissions from shipping: These emissions already account for a large fraction of NO_x in the European airshed and are, according to scenarios, expected to continue to increase, possibly by as much as 50% by 2020 relative to 2000 levels (Cofala *et al.*, 2007).

Further NO_x control from shipping is also important for reducing hemispheric ozone and it may from this perspective also be important to consider the needs for more stringent regulation of methane emissions globally.

Chapter 8 Recovery

Summary

- Recovery of air quality throughout the UK continues, dominated by reductions in sulphur concentrations in air and deposition.
- The deposition of nitrogen (N) in the UK, in oxidised and reduced forms, has changed little over the last 20 years, averaging 350 Gg-N deposited annually, despite substantial reductions in emissions. We do not know the fate of the deposited nitrogen and with little change in deposition, the conditions under which recovery might begin have yet to be established.
- Peak ground level ozone concentrations have declined by approximately 30 ppb (~25%) as a consequence of controls on precursor emissions, mainly in the UK but also in part due to emission reductions more widely throughout Europe. However, background concentrations have steadily increased by approximately 4 ppb over the last 20 years due to increases in emissions of ozone precursors throughout the northern hemisphere. With these changes in the ozone climatology, ground level ozone remains a threat to vegetation, human health and climate.
- Chemical and biological recovery of acidified soils and freshwaters is progressing throughout the UK with reductions in acidity and the reappearance of acid-sensitive biota in freshwaters, and reduced acidity in soils. However, the end-point of the recovery trajectory remains unclear and could differ significantly from pre-acidification as a result of changes in climate, land use and future levels of N deposition.
- Large areas of the UK remain in exceedance of critical loads for acid deposition; exceedances are expected to decline over the coming decade from 54% of UK habitats in 2006-08 to 40% in 2020.
- Soils, freshwaters and vegetation show no significant signs of recovery from the widespread effects of eutrophication. Current (2006-08) exceedances of critical loads for eutrophication amounting to 58% of UK terrestrial habitats by area are expected to decline to 48% by 2020. Rates of biogeochemical recovery in terrestrial systems are expected to be much faster than recovery rates in higher plants. Experience from other countries such as the Netherlands shows that active management is required to restore sensitive habitats.
- Reductions in sulphur dioxide concentrations have led to a recolonisation of large areas of the country by sensitive lichen and bryophyte species, but total species numbers have not reached levels recorded before impacts began.
- Foliar sulphur concentrations of major tree species, grassland and crops have declined in response to reduced sulphur deposition, and in some cases have now reached deficiency levels.
- Climate change may influence the processes driving acidification (and recovery), eutrophication and ground level ozone but, where evidence is available, there are both negative and positive interactions.
- The quantity of metals, such as copper and lead, strongly retained in soil following atmospheric deposition will decline very slowly, taking hundreds of years to respond to recent reductions in deposition. However, the amounts

of less strongly bound metals in soil, including nickel, zinc and cadmium, will decline in response to reductions in deposition during the present century. A consequence of these long time constants for the soil processing of metals is that the main problems of soil contamination by metals in the UK are a legacy of historical deposition. However, current deposition of copper, lead and zinc still presents a threat to the soils of some woodland habitats.

8.1 Introduction

Among the objectives of this report, few have higher priority than the following two questions: How have the UK atmosphere and terrestrial ecosystems responded to the large reductions in emissions of gases responsible for acidification, eutrophication and ground level ozone over the last twenty years? and, given the analysis of trends in this report, what is the likely trajectory for recovery over the coming decade and beyond? It is necessary to answer these questions to advise on the research and monitoring priorities which are addressed in the recommendations in Chapter 9.

This analysis is supported by data from UK monitoring networks established in the mid-1980s that, despite shortcomings, are among the best in Europe, and a range of field surveys and experimental studies to identify the effects and establish quantitative links with causal agents. The UK research and monitoring community has been brought together in this review of a unique and rich dataset. This brief chapter presents a summary of the observed recovery to date and quantifies changes expected over the coming decade.

8.2 Recovery of air quality in the UK

Emissions of sulphur (S) in the UK and more widely in Europe have declined by 94% and 80% respectively since peak emissions in the early 1970s. Oxidised nitrogen emissions have also declined, in the UK by almost 50% and over Europe as a whole by 40%. In the case of reduced nitrogen, emissions have also declined but by much smaller amounts, in the UK by 21% and over Europe by 30%, although two countries, the Netherlands and Denmark, have reduced ammonia emissions by larger amounts (40% and 35% respectively). Emissions of volatile organic compounds (VOCs) declined by 70% in the UK and by 65% over Europe since the peak in the late 1980s. These reductions bring the UK national emissions below National Emission Ceilings Directive (NECD) targets for all these pollutants.

Chapter 3 discusses the changes in concentrations and deposition occurring as a result of changes in emissions (Chapter 2). Reductions in emissions lead to reduced ambient concentrations of the primary pollutants (in particular sulphur dioxide (SO_2) and NO_x), which have declined to concentrations that present no direct threat to UK ecosystems except at some urban locations. At sites in the east Midlands, which were heavily polluted in the 1960s and 1970s, concentrations of SO_2 have declined by 90%, from 50 $\mu g\ m^{-3}$ in 1967 to 4 $\mu g\ m^{-3}$ in 2002, but the decline varies greatly throughout the country.

Concentrations of aerosols in the UK have also decreased in response to emission reductions (AQEG, 2005), especially in urban areas but also more widely over the UK.

The composition of aerosols has also changed considerably, with very large reductions in black carbon emissions in the 1960s and 1970s following the Clean Air Act (1956), and large reductions in sulphur emissions over the last three decades (see Figure 2.1). The inorganic aerosol composition has changed from one dominated by sulphate (SO_4^{2-}) at regional scales, to one dominated by ammonium (NH_4^+) and nitrate (NO_3^-) in recent years. Organic compounds have been shown to make an important contribution to aerosol composition, but only in the last few years have measurement systems been available to provide quantitative detail (AQEG, 2005; Zhang *et al.*, 2007).

There are no longer exceedances of critical levels for ecosystem effects for SO_2 and nitrogen dioxide (NO_2) (except in some urban areas) and while the human health effects of atmospheric aerosols represent an important target for improvement, greatly reduced ambient concentrations have substantially reduced the risks of effects on human health. The exception as a primary pollutant is ammonia (NH_3), for which, with important developments in understanding in recent years, substantial areas of the UK are showing exceedance of critical levels.

8.3 Recovery from acidification

The large improvements in air quality and the absence of direct effects of the primary gaseous pollutants SO_2 and NO_2 on UK ecosystems represent important achievements. Current terrestrial effects in the UK are mainly due to secondary pollutants from deposited acidity, nitrogen (eutrophication) and ground level ozone. While reductions in deposition have occurred, substantial areas of critical load exceedance remain. The total sulphur deposition in the UK declined between 1986 and 2006 by 80%, in line with the 80% change in emissions. However, the spatial pattern of deposition changed radically, total dry deposition declined by 94%, whereas wet deposition declined by 58% (Figure 3.11). As a consequence, total deposition declined far more in the southern and eastern areas dominated by dry deposition, than in the northern and western areas dominated by wet deposition. The underlying processes have been investigated in sufficient detail to identify the causes of these non-linearities in the emission–deposition relationship for sulphur over the UK (Fowler *et al.*, 2007b) (as described in Chapter 3).

8.4 Exceedance of acidity critical loads

Reductions in the deposition of acidifying pollutants have reduced UK exceedances of critical loads of acidity from 84% of the total area of sensitive Broad Habitats in 1986-88, to 54% in 2006-08 (Table 8.1). Exceedance maps and summary statistics provide information on the habitat areas at risk from the potential harmful effects of acid deposition on systems in steady state conditions, thus current exceedance of critical loads does not necessarily equate with current damage. Similarly, achievement of non-exceedance of critical loads does not necessarily mean that affected systems have recovered. Timescales for recovery may be long, particularly for very sensitive habitats, and chemical recovery (e.g. soil chemical status) will not necessarily lead to immediate biological recovery (e.g. soil biota). Dynamic models are used to assess the timescales for recovery and the associated changes in chemical status; an example of the modelled chemical recovery of heathland soils is provided in Section 8.5.

Table 8.1: Summary of critical loads exceedances of habitats in the UK for acidification and Eutrophication. Source CEH/RoTAP.

Broad Habitat	Percentage habitat area with critical loads exceeded by deposition data for:							
	Acidity				Eutrophication			
	1986-1988	1996-1998	2006-2008	2020	1986-1988	1996-1998	2006-2008	2020
Acid grassland	95.9	90.2	79.9	68.0	65.3	68.7	57.9	40.4
Calcareous grassland	9.1	0.0	0.0	0.0	79.1	78.6	50.3	19.6
Dwarf shrub heath	92.7	66.9	36.9	22.4	34.0	36.3	29.9	20.7
Bog	99.9	91.2	75.0	45.7	44.7	45.8	51.6	40.1
Montane	99.9	94.7	88.1	76.5	97.5	92.1	97.3	91.5
Managed conifer	85.1	78.7	65.2	50.9	92.7	94.4	94.1	87.4
Managed broadleaved	78.6	76.1	62.8	48.6	97.9	98.2	97.9	96.7
Unmanaged wood (ground flora)	76.7	70.1	49.0	35.9	95.9	96.3	96.2	94.7
Atlantic oak (epiphytic lichens)					95.9	97.2	96.5	87.3
Supralittoral sediment	N/A	N/A	N/A	N/A	26.7	38.5	14.9	3.9
Freshwaters*	39.7	29.5	20.9	15.3	N/A	N/A	N/A	N/A
All habitats	83.9	71.3	53.7	40.1	62.3	64.2	58.4	47.8

*Percentage of the catchment areas of 1752 sites sampled across the UK

The changes in the spatial distribution of acidity critical load exceedances since 1986 are shown in Figure 8.1. With current deposition (2006-08), the highest areas of exceedance (>2.0 keq ha^{-1} yr^{-1}) are restricted to areas of Cumbria, the Pennine hills and South Wales. In the 1980s, high exceedances were widely distributed in the uplands of England, Wales and Scotland, as well as some lowland areas of East Anglia and the Weald. Decreases in the area exceeded over this time (Table 8.1) are largest for dwarf shrub heath (56% decrease), unmanaged woodlands (29% decrease) and bog (25% decrease) habitats. Greater reductions in the area exceeded are more generally seen in the lowlands than in the uplands, reflecting both the larger reductions in deposition in the areas dominated by dry deposition and the greater sensitivity to acidification of soils and freshwaters in upland areas.

Predictions for 2020 show a further 14% reduction in the total area of sensitive habitats exceeded for acidity. For areas still exceeded in 2020, the magnitude of exceedance is predicted to be significantly smaller, with limited areas with exceedance in excess of 1.0 keq ha^{-1} yr^{1} (Figure 8.1d).

The relative contribution of sulphur (S) and nitrogen (N) to acidity critical load exceedance is an important indicator of priorities for control. Using the 2006-08 deposition data the percentage area of habitats exceeded by sulphur alone was just 6.8%, while for nitrogen the equivalent value is 39% (Table 8.2), so clearly nitrogen represents the greatest potential contributor to acidification-related exceedances of habitats in the UK. In the case of potential acidification, nitrogen therefore plays the major role.

Table 8.2: Summary of the relative contributions of sulphur and nitrogen deposition (2006-08) to acidity critical load exceedances in the UK. Source CEH/RoTAP.

Broad Habitat	Percentage habitat area with acidity critical loads exceeded by:		
	Sulphur only	Nitrogen only	Sulphur and nitrogen
Acid grassland	10	66	80
Dwarf shrub heath	8.9	19	37
Bog	6.4	55	75
Montane	18	57	88
Coniferous woodland (managed)	1.5	54	65
Broadleaved woodland (managed)	2.7	53	63
Unmanaged woods	0.02	39	49
Freshwaters	4.0	13	21
All habitats	6.8	39	54

8.5 Dynamic modelling of chemical recovery

The Very Simple Dynamic (VSD) soil acidification model (Posch and Reinds, 2009) has been designed to provide a dynamic model that is compatible with the methods/models used for steady-state critical loads. The VSD model has been widely used by National Focal Centres to provide dynamic model outputs for activities under the Convention on Long-range Transboundary Air Pollution (CLRTAP) (Hettelingh *et al.*, 2008). The UK has participated in these activities and has additionally parameterised the VSD model using deposition scenarios based on the FRAME model; the latter has enabled dynamic model outputs to be generated for the same years as the CBED (1987, 1997 and 2007) and FRAME (2020) critical load exceedance results presented in Section 8.4. Critical loads are calculated to prevent a critical chemical criterion from being violated. To protect the dwarf shrub heath habitat, the chemical criterion used in the UK is a soil solution acid neutralising capacity (ANC) threshold of zero; values below zero represent harm to the habitat (i.e. the criterion is violated). The VSD model predicts soil solution ANC for each time step (1987, 1997, 2007 and 2020), for each 1 km x 1 km square for which dwarf shrub heath is mapped nationally. By combining these ANC maps with critical load exceedance maps for this habitat, different stages of the soil chemical response

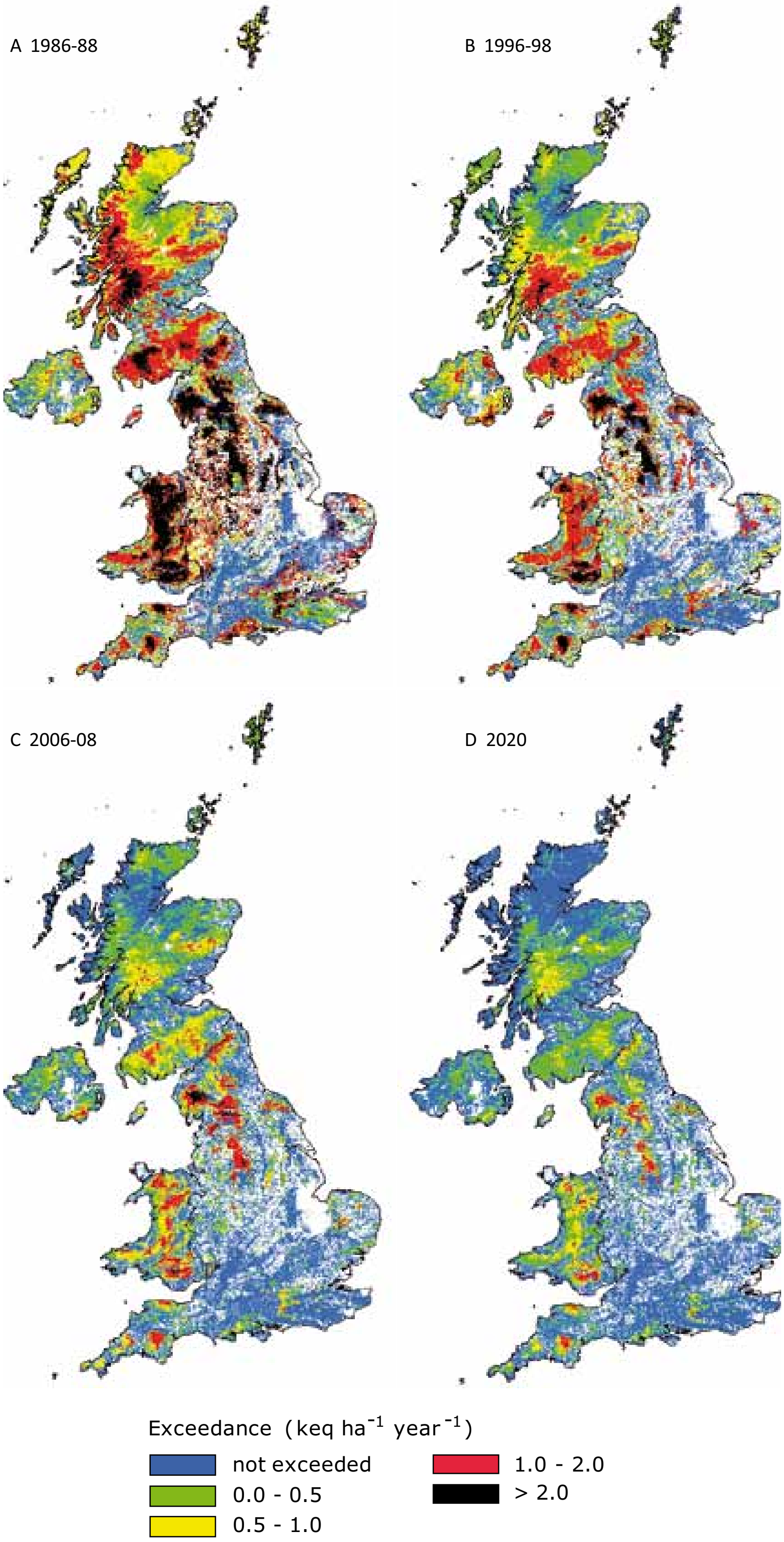

Figure 8.1: Exceedance (keq ha^{-1} yr^{-1}) of 5th percentile acidity critical loads* by CBED deposition in (a) 1986-1988, (b) 1996-1988, (c) 2006-08 and (d) for 2020 from the FRAME model (* Based on critical loads for terrestrial habitats only, i.e. excludes freshwater habitats.). Source CEH/RoTAP.

and recovery can also be mapped (Figure 8.3). First, Figure 8.2 shows five stages of a generalised chemical, biological and critical load exceedance response to changes in acid deposition over time. Biological criteria are not included in the VSD model, but they are included in this figure to demonstrate the principle. The five stages (UBA, 2004) are:

Stage 1: Deposition is below the critical load and chemical and biological criteria are not violated. The ecosystem is safe from harmful effects whilst deposition remains below the critical load.

Stage 2a: Deposition is above the critical load but chemical and biological criteria are not violated as the capacity of soils to buffer acidification has not yet been depleted. This is referred to as the 'Damage Delay Time' (DDT) (Posch and Reinds, 2009). In stage 2b the chemical criterion is violated but the biological criterion is not yet violated.

Stage 3: Deposition is above the critical load and chemical and biological criteria are violated.

Stage 4: Deposition is below the critical load but chemical and biological criteria are still violated. At this time recovery has not yet occurred. The time delay between achieving non-exceedance of critical loads and non-violation of criteria is referred to as the 'Recovery Delay Time' (RDT). In stage 4b the chemical criterion is no longer violated but the biological criterion remains violated.

Stage 5: Deposition is below the critical load and chemical and biological criteria are no longer violated. Only at this stage can recovery be considered to have happened.

Using this general approach Stages 1-5 are mapped in Figure 8.3 for the four time steps (1987, 1997, 2007 and 2020), although it is not possible in the maps to distinguish between Stages 1 and 5. In addition, the areas of dwarf shrub heath habitat associated with each stage for each time step are given in Table 8.3; in this table it has been assumed that habitat areas in Stage 1 or Stage 5 are all in Stage 5. The maps clearly show that in 1987 the majority of the habitat is in Stage 3, (critical loads exceeded and chemical criterion violated), where deposition reductions are required to reverse chemical damage; smaller areas surrounding these are in Stage 2a where critical loads are exceeded but ANC is still above zero. By 1997 some areas in the north-east of Scotland have moved into Stage 4 where critical loads are no longer exceeded but there is a 'recovery delay' until the ANC increases above zero. These are accompanied by areas that have reached Stage 5 and are thus predicted to have begun the process of chemical recovery. The area in Stage 5 increases across Scotland by 2007, but sensitive upland regions of England, Scotland and Wales remain with exceedance of critical loads and violation of the ANC criterion (Stage 3). Despite the gradual changes in spatial patterns, in 1987 and 1997 the majority of the habitat is in Stage 3 (Table 8.3). In 2007 the areas in Stages 3 and 5 are similar, but the area in Stage 4 is higher than in other years, reflecting an increase in the area where critical loads are no longer exceeded, but the ANC criterion remains violated. However, by 2020 58% of the habitat is considered to have recovered with both soil ANC concentrations above zero and non-exceedance of critical loads; though it should be remembered that biological recovery is not included in this analysis. The area of habitat (19%) remaining at Stage 3 in 2020 is restricted to the more acid-sensitive, and largely upland, regions of the country. Further reductions in deposition are required to achieve recovery in these areas.

Table 8.3: Summary of the percentage area of dwarf shrub heath in each 'Stage' class for 1987, 1997, 2007 and 2020. Source CEH / RoTAP.

Stage	Critical load	ANC (criterion)	% Area of dwarf shrub heath by Stage and year			
			1987	1997	2007	2020
	(i)	Not modelled	7.8	7.8	7.8	7.8
2a	Exceeded	Not violated	11.2	9.9	3.8	3.6
3(ii)	Exceeded	Violated	80.2	56.2	32.9	18.7
4a	Not exceeded	Violated	0.1	14.5	20.9	11.9
5(iii)(iv)	Not exceeded	Not violated	0.7	11.7	34.6	58.0

(i) This class is mapped in grey in Figure 8.3 and represents less acid-sensitive areas of dwarf shrub heath habitat (i.e. soil base cation weathering >1.0 keq ha^{-1} yr^{-1}) to which the VSD model was not applied).
(ii) As this analysis is only considering the chemical criterion, this stage incorporates areas in Stage 2b.
(iii) As this analysis is only considering the chemical criterion, this stage incorporates areas in Stage 4b.
(iv) For this table it has been assumed that areas mapped in blue in Figure 8.3 are in Stage 5.

It is important to note that non-violation of a critical criterion does not equate to recovery to reference conditions. Dynamic models also provide insight into the magnitude of chemical recovery, both in the past and in the future. For example, Figure 8.4 (based on the MAGIC model) illustrates that the onset of chemical recovery predated the initiation of monitoring at the Grizedale Forest Level II site, and suggests that current emissions

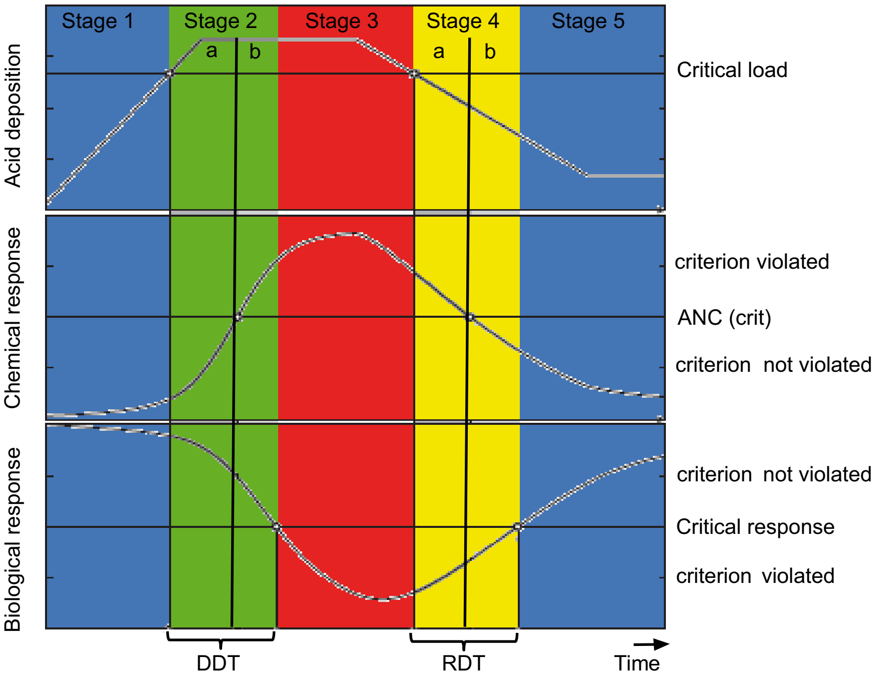

Figure 8.2: The five stages of chemical and biological response to acid deposition (based on Figure 6.1, (UBA, 2004).

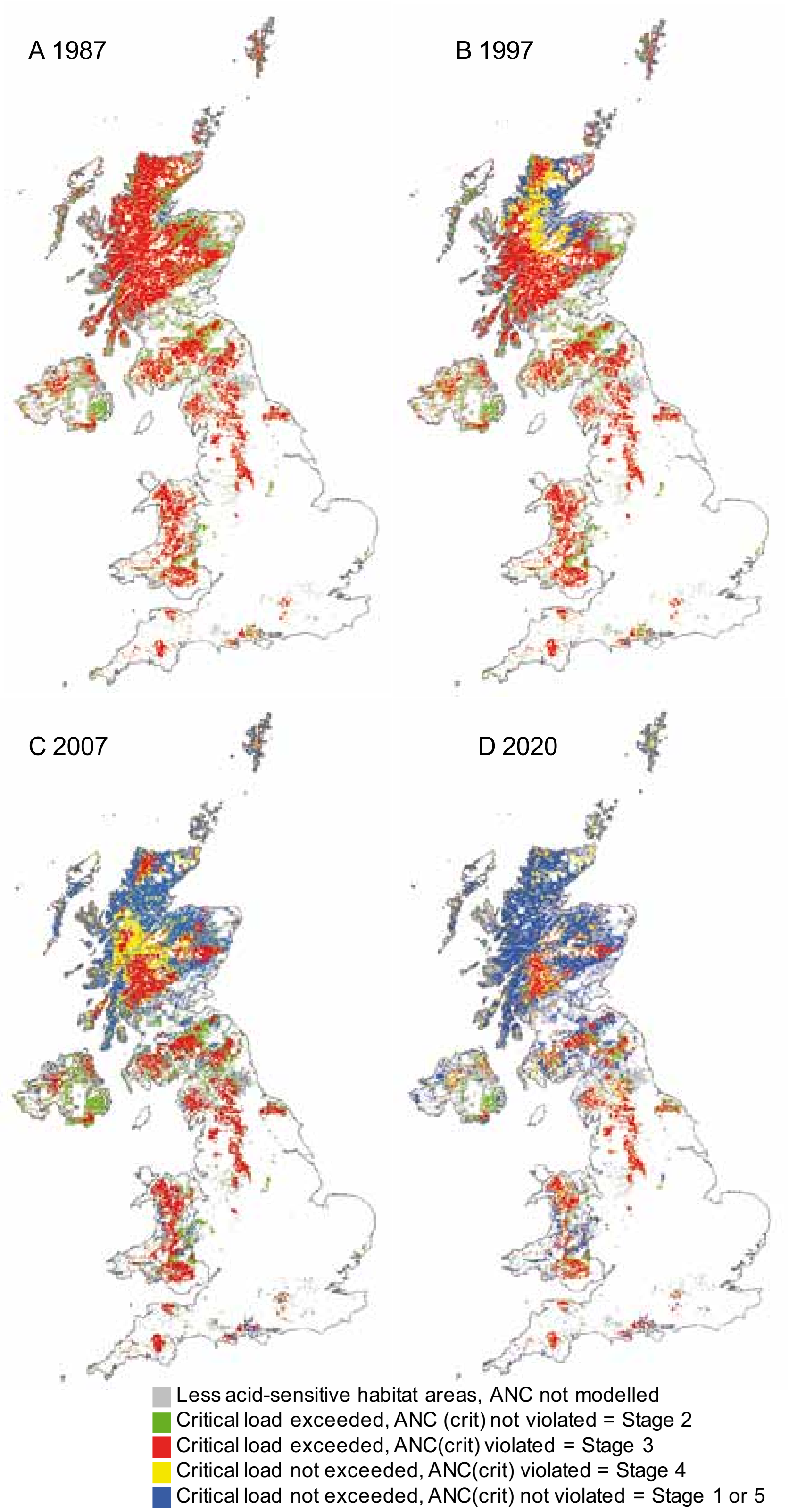

Figure 8.3: Modelled chemical recovery of soil ANC concentrations for dwarf shrub heath habitat in the UK for (a) 1987, (b) 1997, (c) 2007 and (d) 2020. This figure does not incorporate the biological response; hence Stage 3 (yellow) includes Stage 2b, and Stage 5 (blue) includes Stage 4b. Source CEH/RoTAP.

legislation will lead to further modest recovery. Relative to a peak modelled ANC loss of 150 meq l^{-1} at this site, ANC recovery is estimated to be 61% complete at present, and will be 72% complete by 2050 (with ANC remaining below the zero criterion value). While these values will vary considerably by site and ecosystem type, this simulation is illustrative of a general prediction that many soils and surface waters, even if not considered 'damaged' according to the critical loads concept, will remain substantially more acidic than they were under pre-industrial conditions.

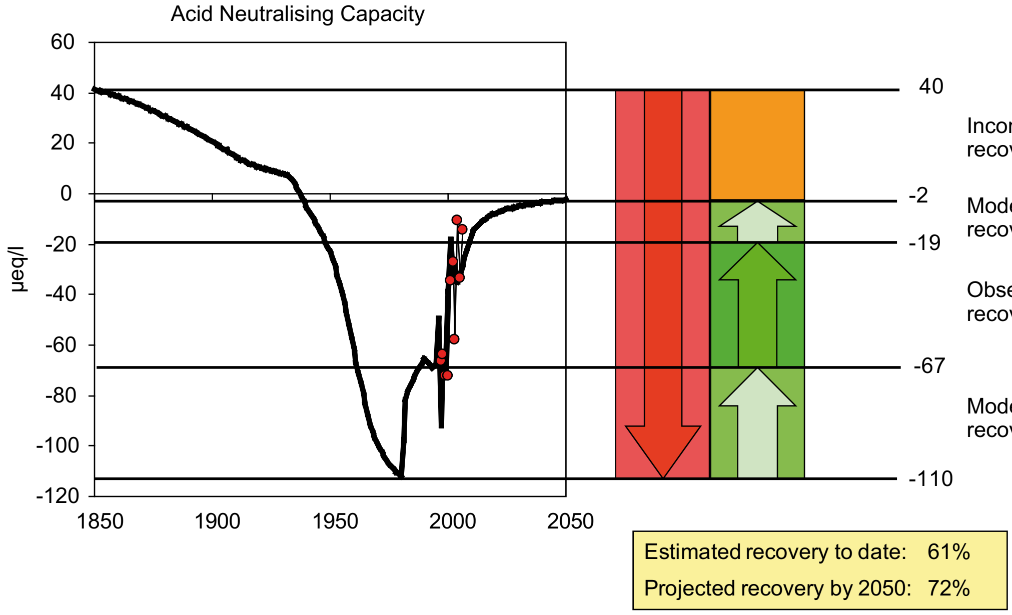

Figure 8.4: Modelled acidification and partial recovery of soil solution ANC at the Grizedale Forest Level II monitoring site. Red dots show observed annual means from 1997 to 2005. Data taken from MAGIC model.

MAGIC has also been applied to 1499 of the 1752 First-order Acidity Balance (FAB) model freshwater sites in the UK (see Section 5.3.7). The results show a substantial but incomplete recovery from acidification from 1970 to 2005, with further recovery predicted under future emission reduction scenarios. Predictions for 2050 show sites with negative modelled ANC to be largely restricted to the North York Moors, southern and central Pennines, Snowdonia and the Lake District. The temporal pattern for modelled nitrate leaching shows an increase in values from 1970 to 2005 attributable to sustained high deposition levels and progressive nitrogen saturation. Only modest reductions in nitrate leaching are predicted under future scenarios.

8.6 Recovery from eutrophication

Despite a 58% reduction in emissions of oxidised nitrogen and a 21% reduction in reduced nitrogen emissions, the total deposition of nitrogen in the UK has changed little over the last two decades, with total annual deposition remaining at ~350 kt-N.

This is surprising given the very large reduction in emissions, as discussed in Chapter 3. There are parts of the UK where reductions in some of the components of nitrogen (N) deposition have declined over the last 20 years by larger amounts than the countrywide statistics suggest, but overall, these reductions are modest. Given the projected emission reductions and cumulative effects of nitrogen deposition on soils it would be unreasonable to expect to see much evidence of recovery in the coming decade.

8.7 Exceedances of critical loads for eutrophication

Given the small reduction in total nitrogen deposition since the mid-1980s (Table 3.2) it is not surprising that this has been accompanied by only a negligible reduction in the percentage area of habitats showing exceedance of eutrophication critical loads (Table 8.1), from 62% in 1986-88 to 58% in 2006-08, a difference which is much smaller than the uncertainty in either value. Current (2006-08) exceedances for eutrophication are similar in area to those for acidification (Table 8.1). The evidence presented in the soils section of the Chapter 5 shows no signs of significant recovery from the effects of nitrogen deposition. Predictions based on FRAME suggest that the total habitat area exceeded for eutrophication will decline to 48% in 2020, with the greatest reductions for calcareous grassland (30% decrease) and acid grassland (18% decrease). However, as for acidity, achievement of non-exceedance of critical loads for eutrophication does not imply recovery of impacted systems.

8.8 Evidence of recovery from survey and related data

The dynamic modelling for dwarf shrub heath (Section 8.5) predicts chemical recovery of soil ANC concentrations in some regions of the UK (particularly north-east Scotland) in response to reduced acid deposition. It would, however, be a surprise to detect chemical and/or biological evidence of recovery from eutrophication given the small scale of the reductions in total nitrogen deposition. In the following sections the evidence of recovery is briefly summarised from the more detailed sections of Chapter 5.

8.8.1 Soils

There have been several surveys of soils in the UK, including those by the National Soil Inventory (NSI) (Kirk *et al.*, 2010) for England and Wales, (Figure 8.4) and by the Centre for Ecology and Hydrology (CEH) as part of the Countryside Survey of the UK (Carey *et al.*, 2008). In both surveys, a consistent decrease in soil acidity and increase in soil pH was observed through the period of the 1970s to the current decade over a range of soil types and habitats (Table 8.4).

The evidence of increases in soil pH are important as soils integrate the longer-term processes of acidification from acid deposition and the effects of weathering of soil minerals.

Table 8.4: Changes in UK soil pH as measured by the Countryside Survey (Carey *et al*., 2008).

	Mean pH		Mean carbon concentration (g/kg)		Direction of significant changes 1998-2007		Direction of significant changes 1978-98		Direction of significant changes 1978-2007	
Broad Habitat	1998	2007	1998	2007	pH	Carbon conc.	pH	Carbon conc.	pH	Carbon conc.
Broadleaved, mixed and yew	5.46	5.75	93.1	80.7	↑		↑	↑	↑	↑
Coniferous woodland	4.40	4.51	201.2	179.1		↓				
Arable and horticulture	6.81	7.20	30.5	27.9	↑	↓	↑		↑	↓
Improved grassland	6.06	6.27	53.2	51.7	↑		↑		↑	
Neutral grassland	6.00	6.14	64.1	61.9	↑		↑		↑	
Acid grassland	4.72	4.78	233.7	208.1		↓	↑		↑	
Bracken	4.48	4.64	142.5	180.7		↑			↑	↑
Dwarf shrub heath	4.50	4.55	271.5	259.5			↑		↑	
Fen, marsh and swamp	5.35	5.46	229.8	208.2			↑		↑	
Bog	4.49	4.51	409.0	393.5			↑	↑	↑	
All vegetation types	5.67	5.87	133.1	124.5	↑	↓	↑	↑	↑	

8.8.2 Freshwaters

Observations of freshwater acidification in Scandinavia and then in other countries, including the UK, provided the main evidence base in the development of concern over acid deposition in the 1970s (Sweden, 1971). The NEGTAP report (2001) provided early evidence of chemical recovery in UK freshwaters, although the effects of acidification were still widespread. Some evidence of biological recovery was presented by NEGTAP, but it was patchy and could be regarded as 'the emerging green shoots'. The evidence now available, reported in Section 5.3, shows widespread chemical recovery in UK acidified freshwaters and substantial evidence of biological improvement. However, as yet, the extent of the improvement in comparison to the reduction in acid deposition that has taken place is limited. The principal conclusions are:

- Almost all of the freshwaters in the UK Acid Waters Monitoring Network show substantial declines in SO_4^{2-} concentration consistent with the reductions in deposition, but sulphate concentrations remain considerably higher than background levels at many sites.

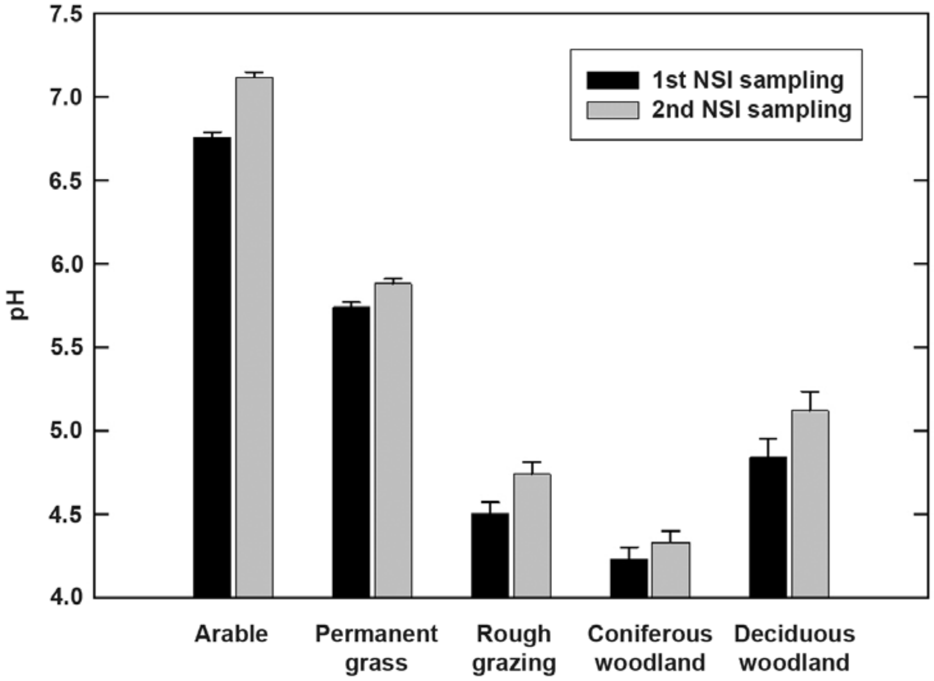

Figure 8.5: Changes in soil pH between 1978 and 2004 from NSI soil sampling (Kirk *et al.,* 2010).

- Changes in freshwater NO_3^- show no clear network-wide trends, consistent with the limited changes in nitrogen deposition. Increases in NO_3^- concentration at a subset of sites could be indicative of progressive nitrogen saturation in catchment soils, and may offset some of the continued improvement expected from SO_4^{2-} reduction.
- A consistent trend of increasing dissolved organic carbon (DOC) in freshwaters draining catchments with organic soil in the UK (and elsewhere) appears to be a natural consequence of the decline in acid deposition.
- The freshwaters showing chemical improvement throughout the UK show concomitant signs of biological recovery, judging from trends in diatom, aquatic plant and macroinvertebrate populations. There are also signs of improvement in fish populations at the most acidified sites.
- However, the biological improvement that has taken place so far is limited. The clearest evidence for this is provided by a comparison between the diatom assemblages found at present and those preserved in lake sediments prior to the onset of acidification in the 19th century.
- The reasons for the limited response to date are not fully understood, but may be related to continuing low pH levels and high aluminium concentrations at the most acidified sites.
- Recovery in future may be influenced not only by trends in acid deposition but also by changes in the behaviour of N in catchment soils, and by land use and climate changes. Future changes in sea-salt deposition in western Britain resulting from climate change could be a significant barrier to long-term recovery from acidification.

- The future of freshwater NO_3^- concentrations and effects remains uncertain and increased leaching of NO_3^- from soil will contribute to acidification and eutrophication.
- The effect of these additional pressures on upland freshwater ecosystems in the UK may lead to the development of surface waters that are ecologically different from those used as reference sites, a consequence that would necessitate a revision of the ecological restoration targets assumed under the EU Water Framework Directive.

8.8.3 Vegetation

The large reductions in SO_2 concentrations that have been observed over the past 30 years have allowed the recovery of a range of sensitive bryophyte and lichen species. However, the process is slow and dependent both on the target species and substrate. Figure 8.6 shows one example where sites in the Peak District, which had been heavily impacted by atmospheric deposition over the last 100 years, were resurveyed in 2005/06 using the same locations and observers as in the early 1980s. The number of moss species increased significantly at both sites, and the liverwort species, which were completely lost in the early 1980s, have recovered. However, species numbers are still well below those expected for pristine conditions; this may reflect the long timescale of recovery or the continued impact of nitrogen deposition in the area.

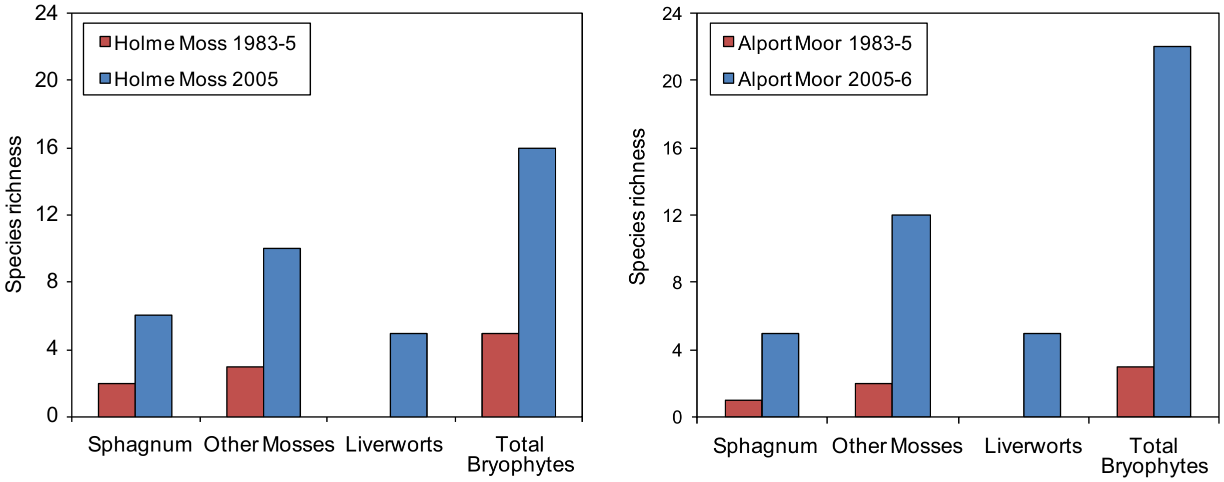

Figure 8.6: Changes in the number of bryophyte species found in monitoring plots at two blanket bog sites in the southern Pennines between 1983-85 and 2005-06 (Caporn *et al.*, 2006).

A further clear signal of declining sulphur deposition is the change in leaf sulphur content. Data from the Forest Research Level II sites show clear evidence of decline in sulphur content over the last 10 years (Figure 8.7). The downward trend in foliar sulphur levels at most sites corresponds to a reduction in soil solution sulphate concentrations. Foliar sulphur levels at some sites, such as the Scots pine Level II site at Rannoch, are now classed as deficient according to van den Berg (1985) and, if the downward trend continues, there is a real possibility that large areas of British woodland could become sulphur-deficient in the foreseeable future (Vanguelova *et al.*, 2007; Vanguelova *et al.*, 2010). Foliar aluminium levels have continued to fall at most of the conifer sites, suggesting a general recovery from acidifying pollutant loading (Vanguelova *et al.*, 2010).

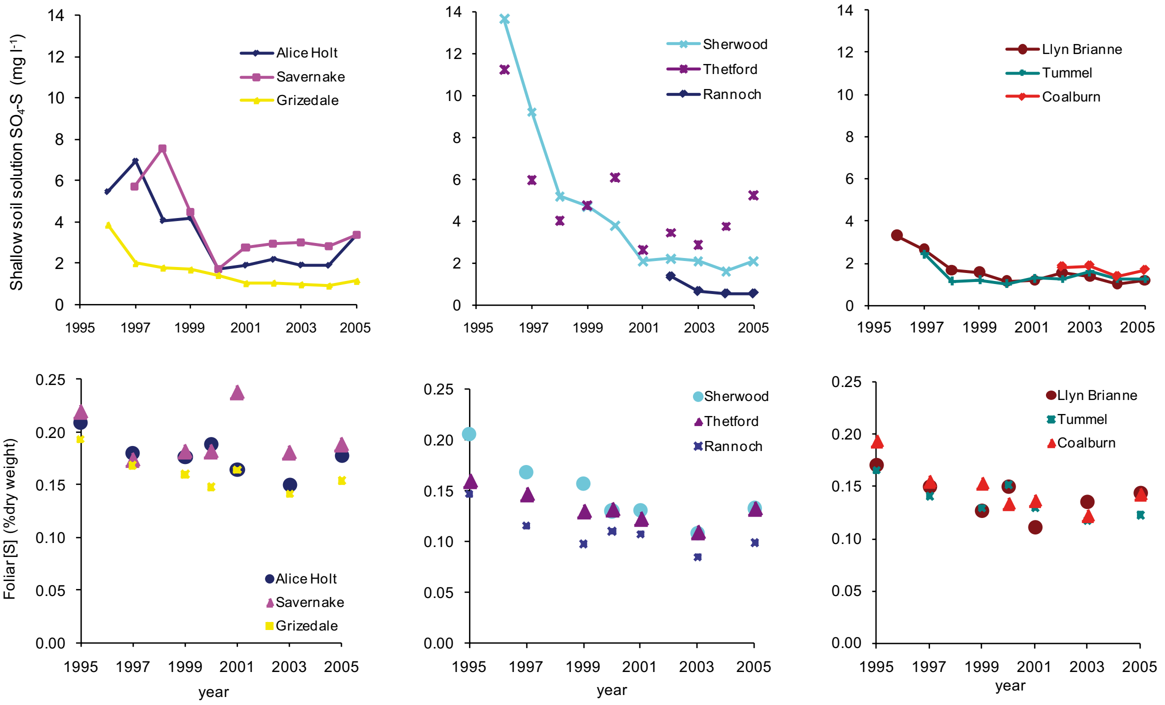

Figure 8.7: Annual mean concentration of SO_4^{2-}-S in (top) soil solution and (bottom) sulphur in foliage for Level II plots of oak (left), Scots pine (centre) and Sitka spruce (right), respectively (Black and grey dotted lines show limits of optimal and deficiency levels respectively.) (Vanguelova *et al.*, 2007).

Similar trends in foliar sulphur content have been observed in unfertilized grassland in the UK as shown in the Park Grass experiment at Rothamsted (Zhao *et al.*, 1998) and in Figure 8.8.

In Figure 8.8, the sulphur content of foliage increases from 2.5 mg g^{-1} in 1860 through to the peak of approximately 4 mg g^{-1} in the 1970s, tracking the long-term changes in sulphur emissions and deposition in the UK. The decline in foliar sulphur from 1980 to the present has brought values back to those experienced in the early days of the industrial revolution, a very rapid recovery. The additional graph in Figure 8.8 of the delta ^{34}S in foliage shows the gradual change in isotope ratio as the combustion-derived sulphur with smaller delta ^{34}S values dilutes the natural (sea-salt) sulphur present in the pre-industrial period. As the anthropogenic sulphur is gradually removed from the ecosystem, the delta ^{34}S is returning to pre-industrial values. Similar trends in foliar sulphur have been observed in cereal crops, which now require fertiliser applications to achieve optimum yield (Zhao *et al.*, 2003).

As described in Chapter 5, critical loads for effects of nitrogen deposition on vegetation are exceeded over much of the UK, and there is little evidence of changes in deposition

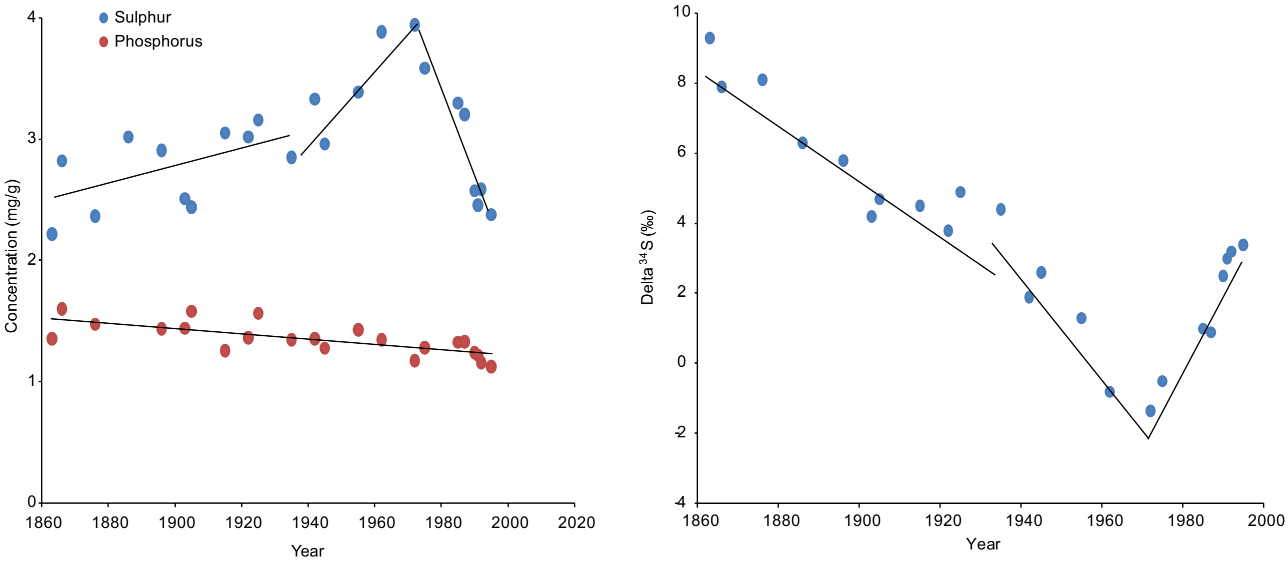

Figure 8.8: Changes in the foliar sulphur and phosphorus concentrations in grass in the control plots of the Park Grass experiment at Rothamsted (Zhao *et al.*, (1998) (Also shown on the figure is a time series in the delta ^{34}S of the foliar sulphur as discussed in the text).

over the last 20 years. This is consistent with the fact that, as described in Chapter 5, resurveys of vegetation composition over the same period have shown little change in frequency and cover of sensitive species. Similarly, there is little evidence of change in foliar N concentrations from UK forest surveys over this period.

Evidence of the possible rate of recovery from any future reduction in N deposition comes from four long-term field experiments where increased N deposition has been simulated (Ruabon upland heath, Thursley Lowland heath, and Wardlow acidic grassland and calcareous grassland; see Chapter 5). These experiments have had nitrogen addition treatments stopped in recent years – either to entire plots, or to half-plots to allow N treatment continuation. Further, a misting tunnel experiment on acidic and calcareous grassland monolith turfs removed from the field has allowed recovery to be studied when subject to below ambient deposition. The duration of recovery period is relatively short (5-12 years) to date, but nonetheless recovery has been observed most noticeably in foliar N concentrations of higher and lower plants (Wardlow and misting tunnel acidic grasslands, Ruabon upland heath, and Wardlow calcareous grassland for higher plant N only). Inorganic N concentrations have shown recovery in the Wardlow grassland soils and in the litter layer at Ruabon upland heath (with some indication of soil percentage N recovery at Thursley lowland heath), while soil pH has shown signs of recovery at Wardlow acidic grassland and Thursley. There is little or only weak evidence of floristic recovery in these systems, though lower plants have shown the clearest signs of recovery at Wardlow acidic grassland and Thursley. Overall, these studies are consistent with biogeochemical recovery occurring before (or being more apparent than) floristic recovery. Reduction of the soil solution NO_3^- concentration in Scots pine forest in highly N-polluted areas such as Thetford over the last twelve years, corresponds to an increase in biodiversity of the ground flora and a significant decrease of Ellenberg N score (Vanguelova *et al.*, 2010).

Recovery of the original species diversity may only be possible with active management intervention. In the Netherlands, for example, where large reductions in ammonium deposition have been achieved in some areas, soil conditions still prevent the establishment of sensitive heathland and acid grassland species, and active management by nutrient removal and lime application is first needed to restore the necessary geochemical conditions (Kleijn *et al.*, 2008). In the Thursley lowland heath experiment, in contrast, the general message is that management through mowing or burning has only a limited impact on the speed of recovery, while the misting tunnel work suggests light availability counteracts some N effects, with lower plants performing better during recovery with increased light availability.

8.9 The future trends in recovery of ecosystems from acidification, eutrophication, ground level ozone and heavy metals

The recovery to date in UK soils and freshwaters from the effects of acidification are clear and, with the continued decline in S deposition, recovery can be expected to continue through the coming decades. The area of sensitive habitats with exceedance of acidity critical loads is predicted to decline from 58% in 2004-06 to 40% in 2020 (Table 8.1). However, this does not necessarily mean that 60% of these habitats will have recovered; for dwarf shrub heath 78% is predicted to have achieved non-exceedance of acidity critical loads in 2020 but dynamic modelling shows that only 58% of the habitat will have achieved chemical recovery (soil ANC concentrations greater than zero) by that time.

Some very acid-sensitive freshwater ecosystems depleted in alkalinity by nearly a century of acid deposition will recover very slowly, and some may never fully recover. It is important to note that the precise direction of biological recovery is sensitive to many factors and it is unlikely that precisely the same species composition will be recovered. In the case of eutrophication there has been little chemical or biological recovery of UK soils, freshwaters or vegetation, and a full explanation of the non-linearities in emission–deposition relationships and their cause at the UK scale is necessary in order to simulate the likely trends in deposition over the coming decade. However, the available modelling through to 2020 suggests a modest decline in nitrogen deposition resulting from expected reductions in emissions of NO_x and NH_3, suggesting that the decline in nitrogen deposition is likely to result in the extent of habitat exceedance declining from 61% in 2004-2006 to 48% by 2020 (Table 8.1). Whether the declining nitrogen deposition is sufficient to compensate for the continued accumulation of nitrogen deposited from the atmosphere on semi-natural vegetation throughout the UK and allow recovery to continue is uncertain. It is equally likely that the long-term accumulation of fixed nitrogen from the atmosphere in UK soils represents a greater threat of long-term effects on biodiversity and ecosystem function.

In the case of ground level ozone the current trends of declining peak values and growing background levels complicate interpretation of terrestrial effects; current average concentrations of O_3 throughout the UK and especially in upland rural areas are now sufficiently large to have effects on sensitive species. Hence assessment of the potential for future recovery from ozone effects critically depends on the assumptions which are made about trends in northern hemisphere background ozone concentrations.

Assessment of the effects of ozone on human health are outside the terms of reference of this report and were not included in the AQEG ozone report (AQEG, 2009). However, the European Environment Agency (EEA, 2007) notes that ground level ozone continues to represent a human health problem in Europe, with 21,400 premature deaths per year associated with ozone (Watkiss *et al.*, 2005). Ozone also has effects on climate; as a greenhouse gas tropospheric ozone captures outgoing long wavelength (thermal) radiation. And through the effects of ozone in decreasing net rates of photosynthetic carbon dioxide (CO_2) uptake by vegetation, ozone also affects climate indirectly (Sitch *et al.*, 2007), further increasing the importance of ground level ozone on climate, as discussed in the recent Royal Society report on ground level ozone (Royal Society, 2008) .

Vegetation throughout the UK was influenced by the very high concentrations of SO_2 in the mid-20th century, but by the time interest in long-range transport of pollutants had led to reasonably comprehensive networks to monitor the pollutants in air and rain, the concentrations had declined to levels that posed a threat in only a few areas. Concentrations of SO_2 are therefore no longer relevant for vegetation effects in the UK. The main focus of this report for vegetation is on the effects of ozone and nitrogen.

The quantity of metals, such as copper and lead, strongly retained in soil following atmospheric deposition will decline very slowly, taking hundreds of years to respond to recent reductions in deposition (Chapter 6). However, the amounts of less strongly bound metals in soil, including nickel, zinc and cadmium, will decline in response to reductions in deposition during the present century. A consequence of these long time constants for the soil processing of metals is that the main problems of soil contamination by metals in the UK are the legacy of historical deposition. However current deposition of copper, lead and zinc still presents a threat to the soils of some woodland habitats.

Chapter 9 Recommendations

The recommendations of the Review of Transboundary Air Pollution are listed below. The priorities are not specified in order of importance, as prioritisation of these recommendations is not a straightforward matter. In principle, the highest priorities are those related to ground level ozone and eutrophication of the UK by deposited nitrogen. The reasons for these priorities are that policy action to reduce acidification, driven mainly by sulphur deposition, is largely complete and the level of understanding of the issues and processes is high. There are substantial areas of the science of ground level ozone and nitrogen deposition and their effects which need to be addressed to fully support policy development; these are identified below. For metals, the risks appear smaller than those associated with ozone or nitrogen deposition. However, a secure scientific foundation is currently lacking, and this is needed to support the development of international agreements to regulate emissions and the evaluation of the risk of effects. While the overall priority areas for further research and monitoring are those on eutrophication and ground level ozone, priorities among the specific actions have been assessed as: *** highest priority; ** high priority; *moderate priority; with lower priority recommendations indicated by no asterisks. While of lower priority, recovery from acidification remains important; very large areas of the UK remain in exceedance of critical loads for acidity, and recovery has been shown to be a slow process.

9.1 Monitoring and assessment of the chemical climate of the UK

Highest Priority

- ***The UK air monitoring networks are considered adequate to detect long-term trends in countrywide concentrations and deposition of the major species contributing to acidification and eutrophication, and of metals and ground level ozone. **We recommend that the networks are maintained with at least the current number of monitoring stations and sampling frequency, to quantify responses to control measures and validate atmospheric transport models through the coming decade.**

- **The deposition of nitrogen (N) throughout the UK, while subject to significant uncertainty, has remained within the range of 350 to 400 kt-N per year over the last twenty years. The lack of a significant decrease in nitrogen deposition in the UK in response to reductions in emissions requires further research to provide a full understanding of the cause(s). **We recommend that these non-linearities in the emission–deposition relationships for oxidised nitrogen compounds be studied further to enable appropriate policy responses.**

- There is considerable uncertainty associated with ammonia emissions, both in terms of how they are calculated, particularly with regard to the emission rates assigned to cattle, and the spatial mapping of emissions from certain livestock categories. **We recommend that further work should be undertaken to improve on reporting mechanisms to help reduce these uncertainties in emissions of ammonia and their predicted effects.**
- As the deposition of nitric acid (HNO_3) has been shown recently to be a substantial contributor to nitrogen deposition in the UK, **we recommend measurements of the dry deposition fluxes of HNO_3 to representative UK land uses, to underpin estimates of national HNO_3 deposition. In addition, we recommend some measurements of the local variability in ambient concentrations of HNO_3 to quantify hot spots of nitric acid deposition.**
- **The importance of international and coastal shipping to sulphur and nitrogen deposition in the UK is substantial and, while for sulphur international controls should bring benefits in the coming decade, this source will probably contribute 30% of oxidised nitrogen deposition in the UK in 2020. **We recommend further evaluation of the role of shipping, and of the benefits from reducing emissions of oxides of nitrogen.**
- **Knowledge of natural sources of volatile organic compounds (VOCs) in the UK is not adequate for the modelling and assessment of ground level ozone. **We recommend that improved, spatially and temporally disaggregated emission inventories and parameterisations for these compounds from UK vegetation (including crops and semi-natural species) are developed.**
- The deposition of ozone to terrestrial surfaces exerts a strong control on ground level concentrations, especially in peak ozone episodes. **A site to monitor long-term ozone deposition fluxes at an appropriate UK location is recommended to underpin developments and assessment of photochemical oxidant modelling in the UK.**
- Inorganic nitrogen deposited in the UK is reasonably well monitored, yet deposition of organic nitrogen from natural and anthropogenic sources remains largely unknown and may contribute substantial quantities of nitrogen in some areas. **We recommend that the contribution of organic nitrogen to total N deposition in the UK is quantified.**
- **Long-range transport, transformation and deposition models are required to integrate knowledge, assess the sources and sinks of pollutants and explore policy options to control acidification, eutrophication and ground level ozone in the UK. **We recommend that a range of models (operating over different spatial scales) available for these purposes are further developed and compared with observed concentrations, fluxes and their uncertainities. The further development and application of complex Eulerian models to support policy on cost-effective strategies to abate emissions of pollutants is recommended.**
- *Background concentrations of ozone in the UK have grown by an average of 0.2 ppb per year over the last twenty years. The cause of this increase remains

poorly known. Further research **is therefore recommended on the factors that affect northern hemisphere mid-latitude background ozone concentrations, including biomass burning emissions, stratosphere–troposphere exchange and intercontinental transport.**

- ** The finding that for most metals, deposition in the UK exceeds the known sources by up to a factor of five shows that the sources of metals in the atmosphere over the UK are largely unknown. **We recommend that a revised metal emissions inventory, consistent with observed concentrations and deposition, is developed.**
- The resuspension of particles through either wind or other mechanical disturbance (such as road traffic) is expected to be a significant component of metal concentrations in air. **We recommend that improvements are made to the estimates of metal emissions and resuspension through assessment of the available measurement data, and further development of models.**
- The presence of elemental mercury from non-UK sources dominates ambient concentrations in air in the UK. However, there are clearly local enhancements to observed concentrations and deposition. **We recommend that the relative importance of global background and UK sources to the concentrations and deposition of mercury in the UK be assessed.**
- *There are important interactions between air pollutants and climate change, and some of the feedbacks remain poorly understood. **We recommend that further investigation of these interactions be made, both with respect to atmospheric processes and land–surface interactions, and taking into account episodic influences such as the large ozone concentrations appearing during temperature extremes (e.g. summers 2003 and 1976).**

9.2 Terrestrial and freshwater effects of acidification, eutrophication, ground level ozone and heavy metals

Highest Priorities

- ***The systematic monitoring of UK soils and vegetation did not commence early enough and currently does not have sufficient spatial coverage and habitat representation to fully quantify changes in the impact of air pollutants on UK soils and vegetation. **We recommend that existing schemes and proposals are reviewed and where appropriate built upon to ensure that ongoing effects and recovery from acidification, nitrogen enrichment, ozone and metal contamination can be reported with accuracy and confidence at UK and Devolved Administration level to assess the success of all relevant air quality emission control policies.**

- *** Atmospheric deposition of nitrogen (N) to the UK has been in the range 350 to 400 kt per year for the last 20 years. Relatively little of this appears to be leaching to freshwaters nationally and much N has accumulated in soils, although in some upland catchments, especially where soils are sparse, fluxes to water can be substantial and ecologically damaging. The longer-term fate of the accumulating store of soil nitrogen and its implications for these systems and surface waters more widely remains largely unknown. **We recommend further research into the fate of deposited nitrogen and possible mechanisms which may release the nitrogen to freshwater or the atmosphere in the future.**
- ***Quantification of the continuing improvements in the chemical and ecological status of acid-sensitive lakes and streams in the UK has been possible through the analysis of long-term datasets from integrated physico-chemical and biological monitoring programmes that also provide information on the impacts of other environmental drivers, notably climate change and land management, on upland ecosystems. **We recommend that integrated monitoring at regional, national and international level is maintained, and that the monitoring of water temperature, water levels and algal biomass is enhanced, to improve understanding of the impacts of interactions between atmospheric pollutants and climate change on upland ecosystems.**
- *** In areas of high nitrogen deposition, significant reductions in total plant species diversity and the frequency of sensitive plant species may have already taken place by the 1980s, with the greatest rates of change in species diversity currently being observed in the areas of low to intermediate nitrogen deposition. Nitrogen has also been found to be limiting phytoplankton production in many upland lakes. The consequences of these effects for associated vertebrate and invertebrate species, and for wider ecosystem function in terrestrial and freshwater ecosystems are uncertain. Planned emission reductions will only reduce the area of sensitive terrestrial habitats in which the critical loads for nitrogen deposition are exceeded from 60% to 49% by 2020. As a consequence of continuing exceedance of critical loads, and continuing impacts on sensitive ecosystems, the UK will not meet its commitments under the Habitats and Water Framework Directives to maintain and improve the conservation status of protected habitats. **We recommend further research to determine the ecological impacts of nitrogen deposition on sensitive ecosystems, the development of tools to assess the ecological benefits of reducing nitrogen deposition in various areas of the country, and the development of methods for active restoration management alongside emission reductions to improve biodiversity and ecosystem function. We also recommend closer integration of policy evaluation for air pollution and biodiversity.**

- *The effects of acidification, eutrophication and ground level ozone on different elements of the environment have tended to be assessed in isolation. The concept of ecosystem services provides a valuable basis for a more integrated assessment of the benefits and disbenefits of changes in atmospheric emissions. **We recommend that future scenario evaluation**

includes an integrated national assessment of the implications for the provision of ecosystem services.

- *The reasons for delays in biological recovery relative to chemical recovery remain poorly known in freshwater and terrestrial systems but may include non-linear ecological processes and/or the role of other drivers such as nutrient N and climate change in both freshwater and terrestrial systems. **We recommend that further research in this area is conducted to provide improved understanding of the recovery process and increased confidence in predictions of long-term outcomes, and to assess appropriate targets and pathways.**
- *Inorganic monomeric (or labile) aluminium concentrations in some lakes and streams, particularly within forested systems, remain at levels that are toxic to a range of aquatic biota, especially salmonid fish. The long-term datasets are only available for Acid Waters Monitoring Network (AWMN) sites and sites monitored by Marine Scotland. **We recommend surface water monitoring continues to include this biologically critical chemical variable**.
- **Recovery from acidification has been shown to have affected concentrations and fluxes of dissolved organic matter, with impacts including smaller than expected increases in freshwater pH, and increasing water treatment costs in some regions of the UK. Risk of nitrate leaching is strongly linked to soil carbon stocks and carbon cycling. **We therefore recommend further research, through use of long-term datasets, experiments and palaeoecological reconstruction, to understand the links between soil acidity, carbon and nitrogen cycling, and freshwater dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and nitrate levels.**
- *Changes in soil pH and rising concentrations of dissolved organic carbon in upland waters may also affect the mobility of a range of industrially derived contaminants, including metals and persistent organic pollutants (POPs) that have accumulated in soils. Furthermore, any exacerbation of upland soil erosion by extreme meteorological conditions, e.g. more intense winter precipitation events, may increase the transport of contaminants from soils to freshwaters and lake sediments and into aquatic food webs. **We recommend new research and monitoring of vulnerable ecosystems to improve our understanding of the new threat from these industrial legacy pollutants.**
- *There is evidence that dry-deposited reduced nitrogen (ammonia, NH_3) has greater adverse effects than dry-deposited oxidised or wet-deposited nitrogen on plant communities. **We therefore recommend that further quantification is made for a wider range of habitats of the relative impacts of reduced and oxidised nitrogen deposition to increase the evidence base for a stronger focus of emission control on ammonia sources.**
- As the AOT40 metric for ozone is flawed for vegetation risk assessment**, we recommend that policy evaluation for ozone should rely on flux-based methods.**
- **Flux-based critical levels for effects of ozone on crop yield and forest growth are exceeded over much of the UK. However, flux-based risk

assessment for ozone is well developed only for a small number of crop and forest species. **We recommend the further development of flux-based methods for application to a wider range of vegetation, and especially to plant communities as well as monocultures.**

- *Reduced growth and flowering of sensitive UK plant species can occur at ozone concentrations that are close to current northern hemispheric background concentrations. **We recommend that there be a focus on hemispheric or global policies to reduce emissions of ozone precursors. We also recommend that dose–response relationships be determined for a wider range of plant species and processes to provide a more detailed evaluation of the implications of further increases in background concentrations.**
- *Research on the impacts of nitrogen deposition and ozone on terrestrial ecosystems has strongly focused on vegetation. The consequences of these changes for associated vertebrate and invertebrate species are uncertain. Nitrogen deposition and ozone may have opposing effects on above-ground carbon sequestration and their effects on long-term soil carbon storage are uncertain. **We recommend that a national assessment is undertaken of the effects of changing nitrogen deposition and ozone exposure on biodiversity and carbon sequestration.**
- Climate change, especially more frequent hot, dry summers, will modify the effects of both ozone and nitrogen deposition. **We recommend the expansion of both experimental and modelling studies to fully assess these interactions.**
- Important progress has been made in developing critical loads methodologies for metals, but there remain important gaps. **We recommend that further assessment is made of the dynamics of changes in metal exposure and risk of adverse effects in UK soils and waters, to support risk assessments based on critical loads and limits, with additional evaluation of the suitability of the critical load approach assessing the effects of mercury deposition in the environment.**

9.3 UK contributions to the international development of control measures for long-range transport

Highest Priority

- ***The UK has contributed substantially to international developments in the science of long-range transport, and in the development of control strategies. **We recommend that the UK science community continues to take an active part in the development of the science and policy implication through monitoring, process research and the assessment of effects, to secure the full value of UK research, and the development of new measures to reduce transboundary and intercontinental air pollution.**

- **Emissions from international shipping significantly influence pollutant concentrations and deposition in UK. **We recommend that the current and future role of shipping in acidification, eutrophication and ground level ozone in the UK be quantified.**
- Transboundary and intercontinental exchange of pollutants continue to grow relative to domestic sources, so that for many of the pollutant issues, a national strategy becomes less effective. Ground level ozone is a notable example of this trend; the control strategies need to be hemispheric in scale to address the background ozone entering the UK. **We therefore recommend that the UK research community extends its interactions with international agencies within Europe and beyond to fully engage in the international development of science and policy.**
- **The emission, transport, transformation and deposition processes of the pollutants contributing to acidification, eutrophication, ground level ozone and metals are all sensitive to changes in climate. **We therefore recommend new research to quantify these interactions and their policy significance.**

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Appendix A: Contributors to the Report

This report has been prepared using input and expertise from all of the contributors listed below. A Core RoTAP group was formed comprising the lead authors for each chapter in the report, with additional chapter-specific input received from members of the Associate RoTAP group. Additional input was received from a group of RoTAP Advisors, comprising representatives from the Devolved Administrations, and the regulatory and conservation agencies. A draft of the report was circulated to interested parties for comment as part of a public consultation exercise, the input from which was gratefully received.

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Appendix B: Outline Details of Models Described in the Report

Table A1 Overview of models – See Chapter 4 for additional information

Name	References	Type	Vertical structure (m)	Horizontal resolution (km)	Emissions (temporal, meteorological and sector)
PCM	Kent and Stedman (2007)	empirical	n/a	1 km	NAEI SNAP sector, annual emissions (NO_x). Point sources include stack parameters.
FRAME	Singles et al.,(1998); Fournier et al. (2004; 2002; 2005a; 2005b); Dore et al. (2006; 2007); Vieno (2006; 2010b); Matejko et al. (2009)	statistical Lagrangian	1 m at surface increasing to 100 m at 2500 m above sea level	1 x 1 km or 5 x 5 km (UK) 50 x 50 km (Europe)	Annual emissions. NAEI SNAP sector (SO_2 and NO_x). Agricultural sector (NH_3). Point sources include stack parameters.
HARM	Metcalfe et al. (2005); Whyatt et al. (2007); Page et al. (2008)	statistical Lagrangian	Three layers: <10 m, 10-100 m, >100 m	Standard model 10 x 10 km for UK, within EMEP 50 x 50 km	Boundary values from STOCHEM. Annual emissions from EMEP grid, nested UK emissions from NAEI SNAP. Emitted species: SO_2, NO_x, NH_3, HCl, PM_{10}. Emission height into 3 layers based on data in inventories.
OSRM	Hayman et al. (2006a; 2006b; 2010)	Lagrangian trajectory	Single boundary layer model with surface conversion algorithm in post-processor to give vertical structure	Notionally 10 x 10km	Daily, monthly and weekly variations of the emissions (a) derived from the NAEI for the UK (and assigned to 8 OSRM sectors) and (b) taken from EMEP for non-UK sources. Emitted species are: NO_x, NMVOC, SO_2, CO. The emission of biogenic VOCs based on a bespoke emission potential inventory.
CMAQ	Review: Byun and Schere (2006) Applications in the UK: Sokhi et al. (2006); Yu et al. (2008)	Eulerian	Typically about 20-30 layers and lowest layer ~30-40 m	European (~50 km), regional (~5 km), urban/local (~1 km)	Annual anthropogenic emissions from EMEP (Europe) and NAEI (UK) by SNAP sectors disaggregated using spatial surrogates and temporal profiles. Biogenic emissions computed online within the meteorological model. Point sources include stack parameters.
Unified EMEP EMEP4UK	Simpson et al. (2003); Vieno et al. (2010b; 2008)	Eulerian	First layer ~90 m, in sigma co-ordinates	50 × 50 km for Unified EMEP and 5 × 5 km for EMEP4UK	Daily, monthly and weekly variations of the emissions for each SNAP sector. Emitted species are: NH_3, NO_x, SO_2, NMVOC, PM_{10}, $PM_{2.5}$, CO.
STOCHEM	Collins et al. (2002; 1997; 1999); Derwent et al. (2006; 2009); Johnson et al. (2001); Stevenson et al. (2006; 2004; 2003)	global Lagrangian	Typically 9 hybrid levels up to ~100 hPa. Lowest level ~1 km thick	5 degrees (~400 km at UK latitudes)	Annual anthropogenic. Monthly varying natural and biomass burning. Biogenic VOC diurnal. Biogenic VOC and lightning NOx linked to meteorology.
UK PTM	Derwent et al. (1996; 2008); Jenkin et al. (2002) (2008); Utembe et al. (2005)	Lagrangian trajectory	Single layer up to top of the boundary layer	10 x 10 km (UK) 50 x 50 km and 150 x 150 km (Europe)	Annual emissions with day-of-week and diurnal variations by SNAP sector. NAEI and EMEP for SO_2, NO_x, NH_3, CO, CH_4 and VOCs, isoprene from EMEP, terpenes from GEIA. 175 VOCs from 248 SNAP sectors.

Name	Land use classification	Meteorological drivers	Dry deposition description	Wet deposition description	Chemical conversion description
PCM	n/a	ADMS hourly met data.	n/a	n/a	Empirical relationship between urban decrement and local NO_x concentrations.
FRAME	CEH land cover (forest, moorland, grassland, arable, urban, water)	UK Met Office mapped annual precipitation. Statistical wind frequency and speed from radiosonde data.	Canopy resistance formulation for gases. Bi-directional exchange option for NH_3.	One coefficient for scavenging process, directional orographic precipitation	20 chemical species, pseudo first order reaction rates, gas and aqueous oxidation of SO_2 to sulphate, gas phase and particulate formation nitrogen chemistry.
HARM	Nine land use types based on CEH land cover data	Annual gridded precipitation from UK Met Office, wind speed and frequency based on UK Met Office Unified model.	Deposition velocities set for each gas for each of 9 land use types, handled simultaneously to maintain mass conservation.	Species dependent wet scavenging, varies patially to represent orographic enhancement	24 trace constituent species, oxidation by O_3, OH and aqueous phase (for S). Nitrate production from NO_2 via HNO_3 and N_2O_5 and from ammonia via HNO_3.
OSRM	For UK, aggregated to five classes (urban, grass, wheat, potatoes, beech) based on UK CORINE land cover dataset	UK Met Office NAME archive.	Resistance approach using aerodynamic resistance and non-aerodynamic terms (with diurnal and seasonal dependence for O_3). Post-processor has more sophisticated treatment for O_3.	Not modelled	Mechanism has 70 species, 200 thermal and photochemical reactions and 12 emitted NMVOCs including isoprene. Derived from STOCHEM scheme with extra reactions added: (i) HONO chemistry; (ii) reactions of peroxy radicals with NO_3; and (iii) formation of organic nitrates. DMS chemistry replaced.
CMAQ	CLC 2000 or USGS	MM5 or WRF or UM.	Improved version of the scheme by Wesely (1989).	RADM algorithms precipitation rate and cloud water concentration dependent	Different chemical mechanisms (CB-IV, CB05, SAPRAC-99 and RADM2) and solvers (EBI, SMVGEAR) are available.
Unified EMEP EMEP4UK	16 land use classes, CORINAIR dataset (Unified EMEP), 30″ USGS dataset (EMEP4UK)	HILRAM NWP model (Unified EMEP), WRF NWP model (EMEP4UK).	Resistances analogy to calculate deposition velocity. Stomata and non-stomata path are calculated.	Scavenging coefficients for in-cloud and below cloud	Includes ozone chemistry and ammonium chemistry, gas and aqueous oxidation of SO_2 to sulphate.
STOCHEM	Uses Unified Model MOSES2.2 scheme, 9 land use classes	Coupled to Hadley Centre climate models or driven from archived Unified Model output.	Resistance model – dependence on aerodynamic resistance and surface vegetation (e.g. stomatal conductance).	Species-dependent scavenging coefficients that differ for convective and dynamic clouds	70 species, 12 emitted NMVOCs including isoprene, aqueous-phase S including DMS.
UK PTM	Not modelled	UK Met Office NAME archive, HYSPLIT/NCEP, BADC/UK Met Office.	Simple dry deposition velocity approach for O_3, NO_2, SO_2, NH_3, HNO_3, H_2O_2, PANs, ROOHs.	Not modelled	MCM v3.1: 4414 species, 12871 reactions, 175 VOCs. MCM CRIv2: 434 species, 1183 reactions, 115 VOCs. CBM4: 36 species, 93 reactions, 8 VOCs.

Appendix C Glossary (with abbreviations and acronyms)

Unit prefixes:

T	tera	10^{12}	c	centi	10^{-2}	k	kilo	10^{3}	n	nano	10^{-9}
G	giga	10^{9}	m	milli	10^{-3}	h	hecto	10^{2}	p	pico	10^{-12}
M	mega	10^{6}	μ	micro	10^{-6}	(u is substituted where the μ character is not available)					

The Encyclopaedia of the Atmospheric Environment (http://www.doc.mmu.ac.uk/aric/eae/index.html) is a comprehensive source of background information on atmospheric issues for non-specialists and many of the definitions given below are taken from it.

acid deposition: The removal of acidic or acidifying compounds from the atmosphere by precipitation (rain, cloud droplets, fog, snow or hail), also known as acid rain or acid precipitation.

acidification: The generation of more hydrogen ions (H+) than hydroxide ions (OH-) so that the pH becomes less than 7.

advection: The movement of an entity by a horizontal flow of air, e.g. pollution carried by wind.

AERO4: Aerosol module used in the CMAQ model. It differs from AERO3 in one key aspect -- AERO4 contains calculations of sea-salt emissions and thermodynamics whereas AERO3 does not. In AERO4, emissions of sea salt from the open ocean are calculated as a function of wind speed and relative humidity. These emissions are speciated into sodium, chloride, and sulfate, and are distributed by size to the accumulation and coarse modes.

aerosols: Solid or liquid particles dispersed in the air, including dust, soot, sea-salt crystals, spores, bacteria, viruses and many other microscopic particles.

Air Quality Archive – Website available at http://www.airquality.co.uk/. The database contains tables of measured concentration data and statistics from the monitoring networks operated on behalf of the Defra and the Devolved Administrations from 1960 until the present day.

Ali: inorganic aluminium

ANC: acid neutralising capacity

AOT40: Accumulated ozone concentration above a threshold of 40 ppb, AOT40 = Σ ($O_3c > 40$) – 40, where O_3c = ozone concentration and the summation is made over a prescribed time period.

AQEG: Air Quality Expert Group. http://www.defra.gov.uk/environment/quality/air/airquality/panels/aqeg/

ASSIs: Areas of Special Scientific Interest, Northern Ireland equivalent of SSSIs

ATMs: Atmospheric Transport Models

AURN: Automatic Urban and Rural Network (UK monitoring network) http://aurn.defra.gov.uk/

AWMN: UK Acid Waters Monitoring Network. www.ukawmn.ucl.ac.uk/

BAP: Biodiversity Action Plan

c. or ca.: abbreviation of circa meaning about/approximately

C: carbon

C:N: carbon:nitrogen ratio

CBED: Concentration-Based Estimated Model

CCE: Coordination Centre for Effects. The CCE is responsible for the development of modelling methodologies and databases for the integrated assessment of effects of air pollution (under climate change) on biodiversity in European natural areas, including Natura 2000 sites. The CCE collaborates with National Focal Centres and many institutions. http://www.pbl.nl/en/themasites/cce/index.html

CCGT: combined cycle gas turbine

CEH: Natural Environment Research Council (NERC) Centre for Ecology and Hydrology. http://www.ceh.ac.uk/

cf.: compare (abbreviation of the Latin confer)

CFV: consumable food value

Cl^-: chloride

CLF: Critical Load Function

CLRTAP: Convention on Long-range Transboundary Air Pollution (http://www.unece.org/env/lrtap/welcome.html). This Convention was the first internationally legally binding instrument to deal with problems of air pollution on a broad regional basis. It was signed in 1979 and entered into force in 1983. It has greatly contributed to the development of international environmental law and created the essential framework for controlling and reducing the damage to human health and the environment of transboundary air pollution. It is a successful example of what can be achieved through intergovernmental co-operation.

CMAQ: The Community Multi-scale Air Quality (CMAQ) modeling system designed to approach air quality as a whole by including state-of-the-science capabilities for modeling multiple air quality issues, including tropospheric ozone, fine particles, toxics, acid deposition, and visibility degradation. In this way, the development of CMAQ involves the scientific expertise from each of these areas and combines the capabilities to enable a community modeling practice. CMAQ was also designed to have multi-scale capabilities so that separate models were not needed for urban and regional scale air quality modeling.

CO_2: carbon dioxide

CORINAIR: acronym for the air emission inventory initially developed in the framework of the European Communities CORINE programme (COoRdination d'INformation Environmentale).

critical level: A critical level is the maximum pollutant concentration a part of the environment can be exposed to without significant harmful effects.

critical load: A critical load is the maximum amount of pollutant deposition a part of the environment can tolerate without significant harmful effects.

CS: the Countryside Survey http://www.countrysidesurvey.org.uk

denitrification: The regeneration of dinitrogen (N_2) or nitrous oxide (N_2O) from nitrate (NO_{3-}).

deposition: Can be either wet or dry. In dry deposition a material is removed from the atmosphere by contact with a surface. In wet deposition material is removed from the atmosphere by precipitation.

Defra: Department for Environment, Food and Rural Affairs. http://www.defra.gov.uk/

DETR: Department of the Environment, Transport and the Regions, predecessor of Defra

dissolution: Chemical process by which compounds dissolve into a water droplet.

DMS: Dimethyl sulphide, $(CH_3)_2S$, which is produced in the oceans by microbiological processes and emitted into the atmosphere where it forms sulphate aerosol.

DNMI: Norwegian Meteorological Institute http://www.dnmi.no/

DO3SE: Deposition of Ozone for Stomatal Exchange) is a dry deposition model designed to estimate the total and stomatal deposition (or flux) of ozone (O3) to selected European land-cover types and plant species. http://sei-international.org/do3se

DOC: dissolved organic carbon

DoE: Department of the Environment. This was the UK government department responsible for environmental issues prior to 1997. The relevant department then became DETR, until June 2001 when environmental responsibilities passed to Defra.

DON: dissolved organic nitrogen

dry deposition: see deposition

ECMWF: The European Centre for Medium-Range Weather Forecasts (ECMWF, the Centre) is an intergovernmental organisation supported by 33 States, based in Reading. http://www.ecmwf.int/

ECN: Environmental Change Network http://www.ecn.ac.uk

EMEP: The European co-operative programme for Monitoring and Evaluation of the long-range transmission of air Pollutants in Europe, provides governments and subsidiary bodies under the LRTAP Convention with qualified scientific information to support the development and further evaluation of international protocols on emission reductions negotiated within the Convention. http://www.emep.int/

EMEP4UK: application of the EMEP Unified Eulerian Model at a fine spatial resolution for the UK. The EMEP-UM at 50 km resolution is of high policy interest to Defra since this is the model that is used in the official calculations of transboundary fluxes and concentrations under the Geneva Convention on Long Range Transboundary Air Pollution (CLRTAP).

emissions: Normally refers to the release of primary pollutants directly to the atmosphere by processes such as combustion, although many natural processes also release compounds into the atmosphere, such as DMS from micro-organisms in oceans.

eq H^+: units of equivalents for hydrogen ion (H^+) concentration

et al.: and others (abbreviation of the Latin et alii, et alia, etc.)

EU: European Union (http://europa.eu.int/index_en.htm)

EU15: The first 15 Members of the European Union.

EU27: The 27 countries comprising the European Union, namely Austria, Belgium, Bulgaria, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Latvia, Lithuania, Luxemburg, Malta, the Netherlands, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden and the United Kingdom.

Eulerian model: This type of model treats the atmosphere as a grid of points or boxes. The parameters modelled are calculated for each point then these values are passed between the points for the next calculation step.

eutrophication: An increase in the amount of nutrients in waters or soils.

FAB: First-order Acidity Balance model

FAO: UN Food and Agriculture Organization

FRAME: Fine Resolution Ammonia Exchange model (see Chapter 4)

FRS: Fisheries Research Service

GB: Great Britain (In the context of European Union ozone data reporting GB actually refers to the United Kingdom of Great Britain and Northern Ireland.)

GCM: general circulation model

GCM–CTM: While related general circulation models (GCMs) focus on simulating overall atmospheric dynamics (e.g. fluid and heat flows), a CTM instead focuses on the stocks and flows of one or more chemical species. Similarly, a CTM must solve only the continuity equation for its species of interest, a GCM must solve all the primitive equations for the atmosphere; but a CTM will be expected to accurately represent the entire cycle for the species of interest, including fluxes (e.g. advection), chemical production/loss, and deposition. That being said, the tendency is (especially as the cost of computing declines over time) for GCMs to incorporate CTMs for species of special interest to climate dynamics (especially shorter-lived species such as nitrogen oxides and volatile organic compounds).

GLUE: Generalised Likelihood Uncertainty Estimation (GLUE) framework approach which ha sbeen used in the HARM model

Gothenburg Protocol: The latest protocol to the UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP) which aims for substantial reductions in emissions of sulphur dioxide, nitrogen oxides, ammonia and VOCs to reduce the effects of acidification, eutrophication and ground level ozone.

ground level ozone: Ozone (O_3) present in the lowest layer of the atmosphere, the troposphere, from 0 up to 10 km is called tropospheric ozone. Ground level ozone refers to that in the bottom layer, known as the boundary layer, which is closely coupled to the surface. http://www.unece.org/env/lrtap/multi_h1.htm
h: units of hours
H^+: hydrogen ion
HARM: Hull Acid Rain Model (see Chapter 4)
HCl: hydrogen chloride
HCO_3^-: bicarbonate ion
heavy metals: Generic term used to encompass any metals that can cause effects on human health or the environment. Note that some of the metals included in the definition such as copper and zinc are also essential metals which can lead to effects being caused if the concentration is either too low or too high.
HGVs: heavy goods vehicles
HMDN : Heavy Metals Deposition Network – the rural heavy metals monitoring network, managed by CEH, used to calculate deposition budgets for heavy metals in the UK. http://pollutantdeposition.defra.gov.uk/heavy_metals/
HNO_3: nitric acid
HONO: nitrous acid
ICP Forest - the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests operating under the UNECE Convention on Long-range Transboundary Air Pollution. ICP Forests was launched in 1985 under the Convention on Long-range Transboundary Air Pollution of the United Nations Economic Commission for Europe (UNECE) due to the growing public awareness of possible adverse effects of air pollution on forests. ICP Forests monitors the forest condition in Europe, in cooperation with the European Union using two different monitoring intensity levels. The first grid (called Level I) is based on around 6000 observation plots on a systematic transnational grid of 16 x 16 km throughout Europe. The intensive monitoring level comprises around 800 Level II plots in selected forest ecosystems in Europe. Currently 41 countries participate in the ICP Forests. http://www.icp-forests.org/
ICP Vegetation - The ICP Vegetation was established in 1987 under the United Nation Economic Commission for Europe (UNECE) Convention on Long-Range Transboundary Air Pollution (LRTAP).The ICP Vegetation is an international research programme investigating the impacts of air pollutants on crops and (semi-)natural vegetation and reports to theWorking Group on Effects (WGE). The programme focuses on the following air pollution problems: impacts of ozone pollution on vegetation and the atmospheric deposition of heavy metals and nitrogen to vegetation. In addition, the ICP Vegetation is taking into consideration impacts of pollutant mixtures (e.g. ozone and nitrogen), consequences for biodiversity and the modifying influence of climate change on the impacts of air pollutants on vegetation. The results of studies conducted by the ICP Vegetation are used in assessments of the current, and predictions of the future, state of the environment. Thirty five Parties to the LRTAP Convention participate in the programme. The programme is led by the UK, has its Programme Coordination Centre at the Centre for Ecology and Hydrology - Bangor and is funded by the Department for Environment Food and Rural Affairs (Defra). http://icpvegetation.ceh.ac.uk/
IIASA: International Institute for Applied Systems Analysis
IMO: International Maritime Organization. http://www.imo.org/Pages/home.aspx
IPC: Integrated Pollution Control
IPCC: Intergovernmental Panel on Climate Change, established by the World Meteorological Organization (WMO) and the United Nations Environment Programme (UNEP) in 1988, to examine the science and implications of climate change. http://www.ipcc.gov.uk/
IPPC: Integrated Pollution Prevention and Control
JNCC: Joint Nature Conservation Committee. http://www.jncc.gov.uk/
kt-N: kilotonnes of nitrogen
kt-S: kilotonnes of sulphur
LAEI: London Atmospheric Emissions Inventory. http://static.london.gov.uk/mayor/environment/air_quality/research/emissions-inventory.jsp
Lagrangian model: This type of model takes an initial set of values for a point or parcel of air then moves that parcel through the model domain (e.g. a two-dimensional surface or a three-dimensional box covering a country), modifying the values in the parcel as goes (e.g. adding emissions or changing concentrations due to chemical processes).
LCP: Large combustion plant, any technical apparatus in which fuels are oxidised in order to use the heat generated with an energy output above around 50 Mega Watts.
LRTAP: see CLTRAP
MAGIC: (Model for Acidification of Groundwater In Catchments) is a process-oriented intermediate-complexity dynamic model by which long-term trends in soil and water acidification can be reconstructed and predicted at the catchment scale
MARPOL: Marpol 73/78 is the International Convention for the Prevention of Pollution From Ships, 1973 as modified by the Protocol of 1978. Marpol” is short for marine pollution and 73/78 short for the years 1973 and 1978. Marpol 73/78 is one of the most important international marine environmental conventions. It was designed to minimize pollution of the seas, including dumping, oil and exhaust pollution. Its stated object is: to preserve the marine environment through the complete elimination of pollution by oil and other harmful substances and the minimization of accidental discharge of such substances. Marpol Annex VI amendments came in to force 1 July 2010.
mol: Mole, the quantity of a substance which contains one gram formula weight of the substance. One mole of a substance contains Avogadro’s number (6.0223 x 1023) of molecules or atoms.
MSW: municipal solid waste
N: nitrogen
N_2: nitrogen gas
NAEI: UK National Atmospheric Emissions Inventory. http://www.aeat.co.uk/netcen/airqual/naei/home.html

NAME: The NAME atmospheric pollution dispersion model, first developed by the UK's Met Office in 1986 after the nuclear accident at Chernobyl, which demonstrated the need for a method that could predict the spread and deposition of radioactive gases or material released into the atmosphere. The acronym, NAME, originally stood for the Nuclear Accident ModEl. The Met Office has revised and upgraded the model over the years and it is now used as a general purpose dispersion model.

NAOI: North Atlantic Oscillation Index (Description at: http://www.ldeo.columbia.edu/NAO/; data at: http://www.cru.uea.ac.uk/cru/data/nao.htm)

NECD: National Emission Ceilings Directive

NEGTAP: National Expert Group on Transboundary Air Pollution

NEP: net ecosystem production

NERC: Natural Environment Research Council

NH_3: ammonia gas

NH_4^+: ammonium ion

NH_x: reduced nitrogen, ammonia (NH_3) and ammonium (NH_4^+).

nitrification: The conversion of ammonium ions (NH_4^+) to nitrate (NO_3^-).

NMVOCs: non-methane VOCs

NO: nitric oxide

NO_2: nitrogen dioxide

NO_3^-: nitrate ion

NO_x: sum of the oxides of nitrogen, NO and NO_2

NO_y: total reactive nitrogen defined as the sum of NO_X plus the compounds produced from the oxidation of NO_X which include nitric acid. NO_y component species include NO, NO_2, NO_3, HNO_3, N_2O_5, $CH_3COO_2NO_2$(PAN), and particulate nitrate.

N_2O: nitrous oxide

non-linearities: Refers to the observed non-linear relationship between reductions in primary emissions and reductions in pollutant deposition. It had generally been assumed that a reduction in emissions would lead to a directly proportional decrease in deposition.

NPL: National Physical Laboratory. http://www.npl.co.uk/

NPP: net primary production

NSI: National Soil Inventory. http://www.landis.org.uk/data/nsi.cfm

O_3: ozone gas

OECD: Organisation for Economic Co-operation and Development. http://www.oecd.org/

OH^-: hydroxide ion

OSRM: Ozone Source–Receptor Model

oxidation: The removal of electrons from a chemical species. The species that has lost the electrons is said to be oxidised. The oxidant or oxidising agent is the species that brings about the oxidation by accepting electrons.

P: phosphorus

PAN: peroxyacetyl nitrate

particulates: Particulate matter is a complex mixture of organic and inorganic substances, present in the atmosphere as both liquids and solids. Coarse particulates can be regarded as those with a diameter greater than 2.5 µm, and fine particles less than 2.5 µm. Coarse particles usually contain earth crustal materials and dust from road vehicles and industries. Fine particles contain the secondarily formed aerosols (often acidic), combustion particles and recondensed organic and metallic vapours (from the Encyclopaedia of the Atmospheric Environment).

PCM: Pollution Climate Model

photochemical oxidant: An oxidising chemical formed by photochemistry, e.g. ozone (O_3), peroxy acetyl nitrate (PAN) and hydrogen peroxide.

photochemical smog: Natural and anthropogenic emissions of nitrogen oxides (NO_x) and VOCs can generate other compounds, known as secondary pollutants, through photochemistry. In sunny conditions with warm still air, such as summer anticyclones in the UK, this process can lead to the production of large concentrations of secondary pollutants. This mixture of primary and secondary pollutants is often called photochemical smog.

photochemistry: Chemical reactions driven by sunlight.

photolysis: Decomposition or dissociation of molecules by light (photons).

PM: particulate matter

PM_{10}: particulate matter with a diameter of 10 µm or less. The PM_{10} standard was designed to identify those particles likely to be inhaled by humans, and PM_{10} has become the generally accepted measure of particulate material in the atmosphere in the UK and in Europe.

POD_Y: Phytotoxic Ozone Dose above a threshold of Y. Increasing used in the risk assessment of ozone as a more reliable metric than the AOT_{40}.

POCP: photochemical ozone creation potential

pollutant: Any substance in the wrong place or at the wrong time is a pollutant. Atmospheric pollution may be defined as "the presence of substances in the atmosphere, resulting from man-made activities or from natural processes, causing adverse effects to man and the environment" (see the Encyclopaedia of the Atmospheric Environment).

POPs: Persistent organic pollutants are compounds that persist in the environment, accumulate in the food chain, and pose a risk of causing adverse effects to human health and the environment.

ppb: parts per billion

ppm.h: change in concentration expressed as parts per million per hour.

primary pollutants: Those pollutants emitted directly into the atmosphere, e.g. sulphur dioxide (SO_2).

PTM: Photochemical Trajectory Model

PUMA: The Portable University Model of the Atmosphere is a circulation model in FORTRAN-90 developed at the Meteorological Institute of the University of Hamburg. PUMA originated in a numerical prediction model that was altered to include only the most relevant processes in the atmosphere
RBMPs: River Basin Management Plans
S: sulphur
SACs: Special Areas of Conservation
SCR: selective catalytic reduction
SECAs: SO_x Emission Control Areas under MARPOL Annex VI
secondary pollutants: Those pollutants formed in the atmosphere by chemical reactions, e.g. ozone (O_3).
seeder-feeder effect: Process which enhances the concentration of pollutants in precipitation over hilltops. Hill (orographic) cloud is formed above uplands as the air is forced to rise by the orography. The orographic cloud forms largely within boundary layer air and so contains larger concentrations of pollutants. Precipitation from higher level cloud washes out the hill cloud, increasing rainfall amount and the concentrations of the pollutants reaching the ground (see Chapter 3).
SMB: simple mass-balance model
smog: A term first used to describe sooty or smoky fogs. In the 19th and early 20th century smogs were associated with the burning of coal. In calm weather concentrations of soot particles and sulphur dioxide became concentrated into thick fogs. Photochemical smogs are now more common in the UK as smoke control legislation has greatly reduced emissions of smoke and SO_2.
SMOKE: SMOKE is primarily an emissions processing system designed to create gridded, speciated, hourly emissions for input into a variety of air quality models such as CMAQ, REMSAD, CAMX and UAM. SMOKE supports area, biogenic, mobile (both onroad and nonroad), and point source emissions processing for criteria, particulate, and toxic pollutants.
SO_2: sulphur dioxide gas
SO_4^{2-}: sulphate ion
SO_x: SO_x refers to all sulphur oxides, the two major ones being sulphur dioxide (SO_2) and sulphur trioxide (SO_3).
source sector: A range of angles at a location, usually taken from North, from which an air mass originates, often used to indicate the source of pollution.
SPAs: Special Protection Areas
SSSIs: Sites of Special Scientific Interest, areas of particular value for nature conservation because of, for example, high biodiversity, rare species and rare habitats. Under current UK legislation they are given some protection from development and other forms of disturbance or damage.
SSWC: most commonly used model for estimating freshwater critical loads is the steady-state water chemistry (SSWC) model.
TN: total nitrogen
TORCH: Tropospheric ORganic CHemistry experiment. NERC-funded project comprising two intensive monitoring campaigns measuring a variety of atmospheric pollutants at Writtle College, near Chelmsford, Essex between 27th July - 30th August 2003, and between April and May 2004 at Weybourne Atmospheric Observatory, on the north Norfolk coast. http://badc.nerc.ac.uk/data/polluted-tropo/projects/torch.html
TRACK: TRajectory Model with Atmospheric Chemical Kinetics
UEP38: The Updated Energy Projections (UEP) are published annually by the Department of Energy and Climate Change (DECC). They provide updated projections and analysis of energy use and carbon dioxide emissions in the UK. The UEP exercise incorporates all firm environmental policy measures and is based on updated assumptions consistent with the most recent UK Budget announcements. These projections inform energy policy and associated analytical work across government departments.
UKCIP02:Scenarios used by the Climate Change Impacts Programme. http://www.ukcip.org.uk/
UKTAG: The United Kingdom Technical Advisory Group (UKTAG) supporting the implementation of the European Community (EC) Water Framework Directive (Directive 2000/60/EC). It is a partnership of the UK environment and conservation agencies. It also includes partners from the Republic of Ireland. UKTAG was established in 2001 to provide coordinated advice on technical aspects of the implementation of the Water Framework Directive (WFD).
UKREATE: UK Research on The Eutrophication and Acidification of Terrestrial Ecosystems. Defra funded consortia which is managed by CEH. http://ukreate.defra.gov.uk/
UNECE: United Nations Economic Commission for Europe. UNECE was set up in 1947 and is one of five regional commissions of the United Nations. Its primary goal is to encourage greater economic co-operation among its members. It focuses on economic analysis, environment and human settlements, statistics, sustainable energy, trade, industry and enterprise development, timber and transport. http://www.unece.org/
VOCs: volatile organic compounds, organic chemicals that easily vaporise at room temperature, e.g. benzene.
VSD: very simple dynamic model used to determine soil acidification.
weathering: Chemical weathering is the process by which precipitation dissolves soluble species from rock and so the rock is gradually eroded. Physical weathering processes include the break-up of rock by the expansion of water as it freezes and abrasion by wind-carried material.
wet deposition: see deposition
WFD: EU Water Framework Directive. http://ec.europa.eu/environment/water/water-framework/index_en.html
WHO: World Health Organization
WRF: Weather Research and Forecasting model
yr: units of years
µg m^{-3}: microgrammes per cubic metre

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