Acid Deposition Processes

EPG 1/3/166

Final report to the Department for Environment, Food and Rural Affairs

D. Fowler[a], R.I. Smith[a], M.A. Sutton[a], J.N. Cape[a], E. Nemitz[a], M. Coyle[a], J. Muller[a], C. Milford[a], D. Famulari[a], M.Anderson-Dunn[a], Y.S. Tang[a], R. Storeton –West[a], A. Crossley[a], F. Harvey[a], M. Twigg[a], M. Riedo[a], B. Loubet[a], K. Vincent[b], G. Hayman[b], T. Choularton[c] and K. Beswick[c]

a, Centre for Ecology and Hydrology (Edinburgh Research Station)
Bush Estate, Penicuik, Midlothian, EH26 0QB, UK.

b. netcen
AEA Technology
E5 Culham, Abingdon, Oxon., OX14 3ED, UK

c. Department of Physics
UMIST
PO Box 88, Manchester, M60 1QD,UK

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Report authors: D. Fowler, R.I. Smith, M.A. Sutton, J.N. Cape, E. Nemitz, M. Coyle, J. Muller, C. Milford, D. Famulari, M.Anderson-Dunn, Y.S. Tang, R. Storeton –West, A. Crossley, F. Harvey, M. Twigg, M. Riedo, B. Loubet, K. Vincent, G. Hayman, T. Choularton and K. Beswick	
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EXECUTIVE SUMMARY

Wet deposition monitoring and trends

- The wet deposition network is providing satisfactory concentration and deposition fields for the CL exceedance maps and the detection of trends.
- There are no trends in rainfall amount over the 16-year period from the monitoring sites in the network.
- Wet years show smaller concentrations for pollutant ions than dry years but only NO_3^- and NH_4^+ are statistically significant.
- The North Atlantic Oscillation (NAO) has a minor effect on the rainfall and ion concentrations when averaged over the year. The dry years (negative NAO) tend to have larger concentrations of the pollutant ions and smaller concentrations of marine ions. With the major trends in the concentrations, this is not a dominant effect.
- Acidity in rain has declined by about 50% over the UK since 1986 and the decline is detectable even in the remote regions of the country, but the magnitude in both absolute and relative terms is smaller in the remote areas.
- Concentrations of marine derived ions in rain show a small decline since 1986. The magnitude of the trend is the same at all sites, implying a non-marine cause and is statistically significant only in the English Midlands (group 1) because the magnitude of the change represents a larger fraction of the total at these sites (possibly due to a decline in road salt usage?).
- The trend in non-marine SO_4^{2-} concentration is large and significant throughout the UK and is about 50% of the values in the late 1980s. Even the west coast sites now show clear trends.
- Concentrations of NO_3^- in rain have declined but the trends are significant only in the English Midlands, where it is 20% smaller than 1986, and over this period emissions declined by 50%.
- Concentrations of NH_4^+ in rain declined about 10%, in line with the decline in UK emissions over the 16 years.
- The data for base cations are of poorer quality, and analytical problems during the mid 1990s have reduced the length of the record. However, there is a clear decline in concentrations amounting to about 50% over central and eastern England.

SO_2 concentration monitoring

- The monitoring network now operates with filter pack sampling, which has lower a detection threshold than the bubbler and appears satisfactory for the network.
- Problems of breakthrough in the early phase of the new method have been eliminated and the network is now operating well.
- SO_2 concentrations throughout the UK have declined since 1980, and 1986, the average concentration has declined from about 2 ppb to about 0.2 ppb in 2001.

SO_2 Dry Deposition process studies

- Fluxes of SO_2 have been continuously monitored at two UK sites since 1994 at Auchencorth Moss in Scotland over moorland, and over arable cropland in the English Midlands since 1995.
- At both sites, concentrations of SO_2 have declined, from 1.1 ug SO_2 m^{-3} at Auchencorth Moss in 1995 to 0.8 ugSO_2 m^{-3} in 2001 while at Sutton Bonnington the reduction is larger, from 4 ug m^{-3} to 2 ug m^{-3}.
- The SO_2 deposition fluxes at both sites declined less than concentration because deposition velocities at both sites increased, from 5 to 8 mm s^{-1} at SB and from 4.5 to 6.5 mm s^{-1}at AM.
- The cause of the increase in deposition velocity is a reduction in surface resistance, due to a reduction in the molar ratio SO_2 / NH_3.
- The regional increases in deposition velocity are accelerating the decline in ambient SO_2 concentration and are an important contributor to the changes in S deposition throughout Europe.
- These effects are recognised within EMEP and are parameterised within the EMEP model, improving the model-measurement agreement.

Mapping Methodology and Deposition Maps

- Deposition maps of acidity, sulphur, nitrogen (oxidized and reduced) and base cations have been produced for the period 1998-2000, including significant new methodologies and data for calculation of critical loads and levels.

Total Deposition of Sulphur, Nitrogen, Acidity and Base cations and Trends

- Deposition of non-marine sulphur in the UK has declined from 600kt in 1987 to 190 kt in 2001, a reduction of approximately 70%, during a period in which emissions declined from 1966 kt S to 480 kt S.
- Trends in deposition of oxidized nitrogen are uncertain due to the short period of HNO_3 monitoring. However, trends in precipitation NO_3^- are small, and only statistically significant in the English Midlands. Over the UK, the wet deposition of oxidized N has remained fairly constant at about 100 kt N, dry deposition of NO_2 has declined from about 60 to 30 kt N and the deposition of HNO_3, which is currently about 60 kt N is unknown earlier than 2000.
- Trends in the dry deposition of reduced N appear to have declined by about 10% over the period 1996 to 2000 and wet deposition has declined by about 10% between 1986 and 2001. Overall there does therefore appear to be a small reduction in reduced N deposition over a period in which emissions have declined by about 10%.
- Deposition of non-marine chloride has declined by about 80% between 1986 and 2001, but the absolute values are subject to substantial uncertainty due to analytical problems.

- Base cation wet deposition in the UK declined between 1986 and 2001 by between 30% and 40% and is subject to substantial uncertainty. Dry deposition is uncertain but probably declined by a similar magnitude.

Ammonia measurements

- The environmental consequences of enhanced atmospheric ammonia are being increasingly recognized and include eutrophication of oligotrophic terrestrial ecosystems, acidification of soils and increased atmospheric aerosol loadings affecting atmospheric visibility, global radiative balance and human health.
- International policy instruments are now being developed that include abatement of ammonia, including within the Convention on Long-Range Transboundary Air Pollution, the EU National Emissions Ceilings Directive and the Directive on Integrated Pollution Prevention and Control.
- Fluxes of ammonia between the land and the atmosphere are recognized as being highly uncertain and provide a key limitation to the scientific assessment necessary to underpin the policy developments.
- The NH_3 part of the Acid Deposition Processes project was initiated to provide a focused study and analysis of the biosphere-atmosphere interactions of ammonia under UK conditions in order to improve the quantification necessary to develop sound policy responses. Grasslands were selected as a target ecosystem as they both emit NH_3 to the atmosphere and may be impacted by NH_3 deposition from the atmosphere.
- A substantial effort has been placed in methods development for NH_3 fluxes. New micrometeorological measurement methods have been developed and applied including low-cost gradient methods, a continuous systems for measuring NH_3 fluxes by Relaxed Eddy Accumulation and initial tests with an eddy-covariance system based on TDL-AS. Near source dispersion modelling has also been developed as a new tool for the measurement of NH_3 fluxes.
- The Acid Deposition Processes project has provided the first comprehensive database of NH_3 exchange with grasslands in the UK. The activity represents the international state-of-the-art in NH_3 biosphere-atmosphere exchange.
- The results from the Acid Deposition Processes project have been used to develop a wide range of models including: I) core bi-directional resistance models, II) dynamic models of NH_3 exchange interaction with grassland management and C & N cycling, III) models of within-canopy fluxes, IV) gas-particle inter-conversion models linked to biosphere atmosphere exchange of NH_3, V) short-range dispersion and deposition models, to estimate local sources and establish landscape level interactions through the quantification of advection fluxes.
- The results of the Acid Deposition Processes project are also being used to develop simplified parametrizations of NH_3 exchange that can be used directly in atmospheric transport models. Collaborative work is ongoing to synthesise the UK measurements with other European measurements and to apply the results into the European Monitoring and Evaluation Programme (EMEP) model of the UNECE Convention on Long-Range Transboundary Air Pollution, which will also include efforts to characterize appropriate landcover / landuse maps at the European level. Linked collaboration has also taken place within the EUROTRAC-2 BIATEX sub-project.

- The UK measurements were put into the context of grassland NH_3 exchange across Europe through the linked EU GRAMINAE project, which established a transect of flux measurement stations across Europe. These have used micrometeorological methods and been supported by a series of integrating measurements allowing fluxes to be interpreted and simulated using newly developed numerical models.
- An integrated experiment on NH_3 exchange was hosted in Braunschweig as a core activity of the GRAMINAE programme. This experiment brought together over 50 scientists in the field to consider the interactions of ammonia exchange from the physiological and within-canopy level, to net fluxes and landscape interactions. A key issue in the experiment was the consideration of flux divergence, either due to advection errors or due to gas - particle inter-conversion.
- Through the collaboration with GRAMINAE, which was a component project of the Terrestrial Ecosystem Research Initiative (TERI) and has taken an active role in seeking productive collaboration between TERI projects, the UK results were synthesized in the frame of the TERI Concerted Action (TERICA).
- The UNECE Convention on Long-Range Transboundary Air Pollution is a key user of the results. GRAMINAE has fed directly into several groups of the Convention, including the Ammonia Expert Group, EMEP and the Task Force on Measurement and Modelling.
- Key inputs from the Acid Deposition Processes project to the Ammonia Expert Group include an analysis of the uncertainties linking NH_3 emissions abatement to atmospheric concentrations and deposition, plus inputs to the revision of the Gothenburg Protocol technical Annex on ammonia abatement methods.
- A priority concern highlighted within the Task Force on Measurement and Modelling is the current inadequacy of European NH_3 and NH_4^+ aerosol monitoring, and recommendations have been made to revise the current monitoring strategy.
- A generalised canopy compensation point model for NH_3 deposition has been developed and included in the current FRAME long-range transport model.

Cloud and rain composition monitoring

- Cloud and rain composition measurements at Dunslair Heights show long-term trends downwards in nitrate and non-sea sulphate concentrations, but relatively small changes in recent years.
- There have been large changes over time in the proportion of precipitation sampled as cloud water at Dunslair, most probably caused by the growth of the nearby forest.
- Potential interference by trees has meant that the site has been moved to a similar elevation a few km to the north.
- Cloud and rainfall amounts have increased since 1991 at Holme Moss.
- Concentrations of both nitrate and non-sea sulphate at Holme Moss have decreased in both cloud and rain over the past 5 years.
- There is evidence of source limitation for nitrate deposition at high rainfall (i.e. concentrations decline at the largest rainfall amounts).
- A paper summarising all the results to 2001 has been published (K M Beswick, T W Choularton, D W F Inglis, A J Dore and D Fowler (2003) Influences on long-term trends in ion concentration and deposition at Holme Moss, Atmospheric Environment, Vol 37, pp 1927-1940.)

DELIVERABLES

- Long term trends in SO_2 canopy resistances and deposition velocity for the two sites, reported as i) a chapter of the main report.→ Chapter 3 on "Dry deposition of SO_2"
- Annual update of web pages showing current and past SO_2 concentrations from the UK rural network → www.airquality.co.uk
- Dependence of canopy resistance on surface and atmospheric conditions (surface wetness, temperature, leaf area index) and windspeed, humidity, presence of other gases especially NH_3. Reported as chapter in main report and paper for a peer-reviewed journal. → Chapter 3 on "Dry deposition of SO_2" and Paper: e.g.

  Fowler, D., Sutton, M.A., Flechard, C., Cape, J.N., Storeton-West, R., Coyle, M. & Smith, R.I. 2001. The control of SO_2 dry deposition on to natural surfaces and its effects on regional deposition. Water Air Soil Pollution: Focus, 1, 39-48.
- Annual net NH_3 exchange at 3 sites with different vegetation and pollution climate as report → Chapter 5 on "Ammonia Measurements"
- A generalised canopy compensation point model for NH_3 deposition to short semi-natural vegetation, forest and agricultural crops → Chapter 5 on "Ammonia Measurements" (Section 5.5) and Executive Summary
- Annual 5 km x 5km maps of SO_2, NO_2, NH_3, HNO_3, aerosol SO_4^{2-}, NO_3^- and NH_4^+ concentrations needed to calculate deposition, as below on website www.atmosci.ceh.ac.uk
- Annual 5 km x 5 km dry deposition maps SO_2, NO_2, NH_3, HNO_3, aerosol SO_4^{2-}, NO_3^- and NH_4^+ → as below available on website www.atmosci.ceh.ac.uk
- A summary of the state of the dry deposition models (2003), the changes made during the contract period and the effect of the changes on long term dry deposited trends→ Chapter 2 on " The Rural SO_2 Monitoring Network" (Section 2.5.4)
- Annual cloud chemistry and deposition measurements at 2 upland sites in the UK, for 2002→ Chapter 6 on "Monitoring of cloud and rain chemistry at high elevation"
- Analysis of changes in cloud composition 1986-2000 and separation of meteorology from pollutant source changes during the monitoring period→ Chapter 6 on "Monitoring of cloud and rain chemistry at high elevation"
- Assess critical loads exceedance due to orographic cloud deposition at 5 km x 5 km resolution→ Chapter 4 on "Mapping Methodology and Deposition Maps"
- Maps of NH3 concentration, deposition and UK atmospheric budgets for 2000, 2001→ available on website www.atmosci.ceh.ac.uk
- Maps of UK wet deposition of S, N, Cl, H, Na, Mg for 2001 (depending on supply of UK precipitation fields)→ available on website www.atmosci.ceh.ac.uk
- Deposition Maps provided on web site (Deposition 2001) → www.atmosci.ceh.ac.uk (Pages on Deposition Effects, Measurement, Mapping and Modelling)

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Acid Deposition Processes:

Wet Deposition Monitoring and Trends.

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D. Fowler Ron Smith, Garry Hayman, Keith Vincent, Neil Cape, Jennifer Muller,

Centre for Ecology and Hydrology
(Edinburgh Research Station)
Bush Estate, Penicuik,
Midlothian, EH26 0QB, UK.

netcen
AEA Technology
E5 Culham, Abingdon
Oxon., OX14 3ED, UK

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- The trend in non-marine SO_4^{2-} concentration is large and significant throughout the UK and is about 50% of the values in the late 1980s. Even the west coast sites now show clear trends.
- Concentrations of NO_3^- in rain have declined but the trends are significant only in the English Midlands, where it is 20% smaller than 1986, and over this period emissions declined by 50%.
- Concentrations of NH_4^+ in rain declined about 10%, in line with the decline in UK emissions over the 16 years.
- The data for base cations are of poorer quality, and analytical problems during the mid 1990s have reduced the length of the record. However, there is a clear decline in concentrations amounting to about 50% over central and eastern England.

`1. WET DEPOSITION MONITORING AND TRENDS

1.1 Changes in concentration and deposition 1986 to 2002

The temporal record of composition of air and precipitation in the UK, using a consistent sampling protocol and chemical analysis is now 16 years, and is long enough to overcome most of the inter-annual variability in weather. The record provides very clear and in some cases very large trends with time in concentration and deposition since 1986. During this period, substantial changes in emissions of sulphur dioxide, in the UK and more widely in Europe have occurred, but there have also been climatalogical changes, including the North Atlantic Oscillation (NAO). In this chapter the observed changes in air and precipitation chemistry are presented along with concurrent trends in emissions of sulphur and nitrogen compounds and indices of trends in atmospheric circulation over NW Europe.

The original network (Table 1.1) contained 59 stations but this was reduced in1988 to 32 and is currently 35. The sites are located away from major local sources of contamination, (pollution sources, roads), and are in rural locations, primarily at low altitude, to avoid losing samples in snowy weather, and also to minimize the sampling loss due to exposure of collectors.

It is convenient to consider trends in each of the major ions and rainfall before examining the UK budgets.

Table 1.1. Acid deposition sites (sites considered with more than 10 years of record for ions, with more than 15 years of record for rain, sites in italics are new running sites)

Group	Site	Ref Number	Eastings	Northings
1	Stoke Ferry	5004	570	298.8
1	High Muffles	5009	477.6	493.9
1	Preston Montford	5023	343.2	314.3
1	Flatford Mill	5024	607.7	233.3
1	Thorganby	5117	467.6	442.8
1	Jenny Hurn	5118	481.6	398.6
1	Wardlow Hay Cop	5120	417.7	373.9
1	Bottesford	5121	479.7	337.6
1	Woburn	5127	496.4	236.1
1	Compton	5129	451.2	180.4
1	Driby	5136	538.6	374.4
2	Barcombe Mills	5007	543.7	114.9
2	Glen Dye	5011	364.2	786.4
2	Whiteadder	5106	366.4	663.3
2	Redesdale	5109	383.3	595.4
2	Bannisdale	5111	351.5	504.3
2	Cow Green Reservoir	5113	381.7	529.8
2	Hillsborough Forest	5149	136.9	515.6
3	Yarner Wood	5008	278.6	78.9
3	Goonhilly	5003	172.3	21.4
3	Eskdalemuir	5002	323.5	603.2
3	Loch Dee	5107	246.8	577.9
3	Beddgelert	5119	255.6	351.8
3	Balquhidder 2	5152	254.5	720.7
3	Pumlumon	5150	282.3	285.4
3	Tycanol Wood	5123	209.3	236.4
3	Llyn Brianne	5124	280.7	249.2
3	Achanarras	5140	315.1	955
4	Polloch	5151	179.2	768.9
4	Lough Navar	5006	19.2	521.2

4	River Mharcaidh	5103	287.6	805.2
4	Strathvaich Dam	5010	234.7	875
	Llyn Llydaw	*5153*	*263.8*	*354.9*
	Crai Reservoir	*5154*	*288.2*	*221.9*
	Beaghs Burn	*5155*	*156.7*	*643.2*
	Loch Chon	*5156*	*242.9*	*708.4*
	Loch Nagar	*5157*	*325.2*	*785.9*
	River Etherow	*5158*	*412.5*	*398.6*
	Scoat Tarn	*5159*	*315.8*	*510.3*
	Llyn Llagi	*5160*	*264.7*	*348.3*
	Balquhidder	*5200*	*252.1*	*720.6*

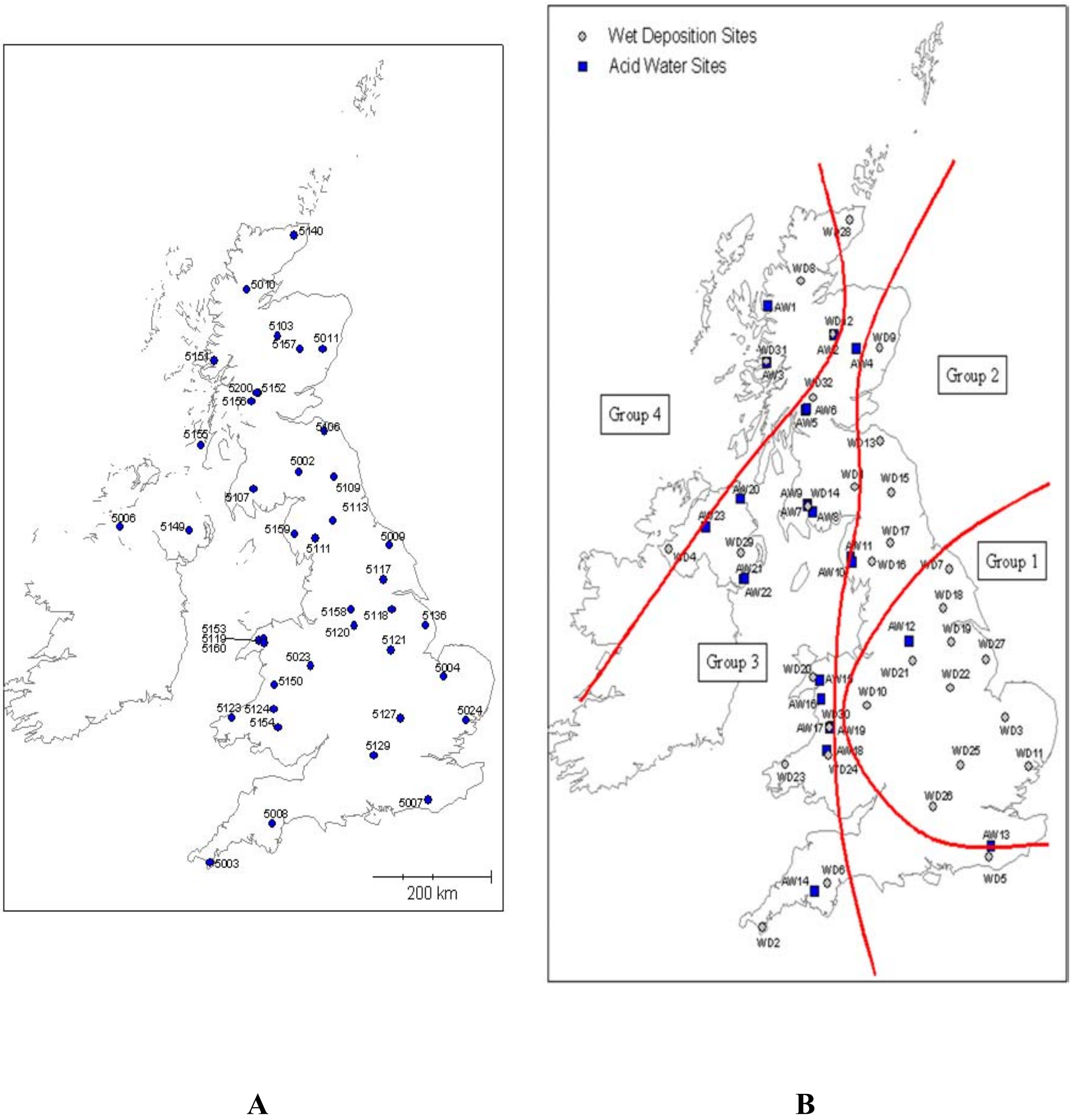

Figure 1.1. Acid Deposition Sites (A) and the geographical locations of groups as in Table 1.1 (B)

1.2. Rainfall

The 28 stations with 15 or 16 years data show no significant trend in precipitation over the sampling period, although the year-to-year variability is considerable as expected in precipitation data (Fig 1.2.). The years 1992, 1998 and 2000 were wet years while 1996 was dry, relative to the mean for the period. A statistically significant relationship between rainfall for the year and ion concentration can only be found for nitrate and ammonium (Table 1.2.).

Table 1.2. Relationship between mean ion concentrations in rain and mean rainfall amount in the UK

	Slope	R^2	p-value
Na^+	-0.02082	0.013	0.669
SO_4^{2-}	-0.01965	0.037	0.478

Cl^-	-0.0241	0.012	0.690
xSO_4^{2-}	-0.01686	0.031	0.517
xCl^-	0.00021	0.000	0.987
NO_3^-	-0.018085	0.360	0.014
NH_4^+	-0.032331	0.499	0.002

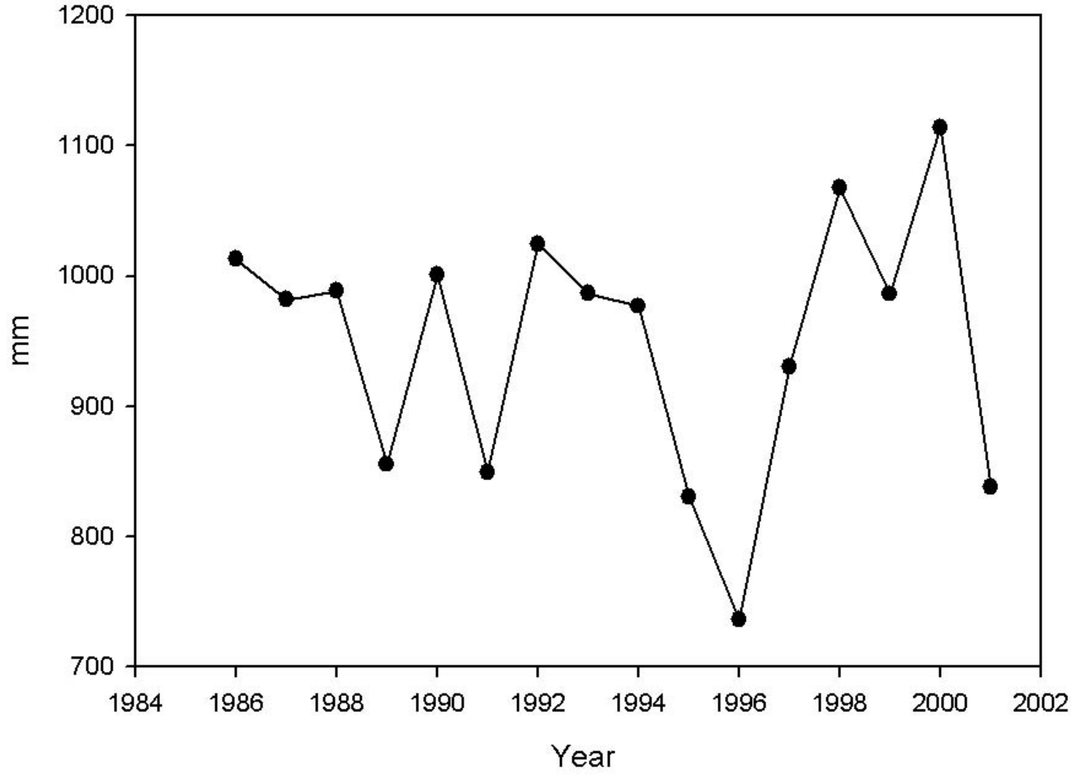

Figure 1.2. Mean annual rainfall for acid deposition sites (n = 28)

Table 1.3. Grouped rainfall statistics (Trends with time)

	Correlation equation	R^2	p-value
Group 1	y = 3.83x -7057	0.034	0.495
Group 2	y = 3.17x -5324	0.01	0.715
Group 3	y = -8.42x +18131	0.094	0.249
Group 4	y = -2.45x +6034	0.05	0.795
Mean	y = -1.01x +2972	0.02	0.859

The location of the UK at the NW boundary of Europe, and with the Atlantic Ocean to the west and Europe to the south and east make the air chemistry very sensitive to air mass trajectories associated with the precipitation. Thus the degree of ‘westerlyness’ for individual years significantly influences the annual deposition pattern of both marine and anthropogenic ions, as described in the 1988 to 1998 report (Monteith and Evans 2000). The peak in the positive values of the NAO, due to larger than average pressure gradient between the Azores and Iceland, is associated with south westerly airflow over the UK, higher wind speeds and the potential for larger marine ion contribution to precipitation chemistry over the UK. In the earlier report, a peak in Cl at many sites in the network in the early 1990s seems consistent with the peak in NAO and high rainfall. Similarly the much smaller than average rainfall and Cl in 1996 occurs in the year with the most negative NAO, and is a year in which the westerlyness is at a minimum. To take the argument further, it is necessary to examine individual events throughout the monitoring period and the relative frequencies of trajectories over different sources to show the extent to which the relative frequencies have changed with time. Such an exercise is not possible using the two weekly sampling protocols. However, it is clear that there have been changes in the climate during the monitoring period, which significantly influences the precipitation amount and composition. With the magnitude of the changes in sulphur emissions and deposition, the main signals are still clear, but for some of the ions for which concentrations and deposition have changed little, these changes of general circulation cause changes in the trajectories, and therefore concentrations of a similar magnitude to the changes in emission (e.g. for NH_3)

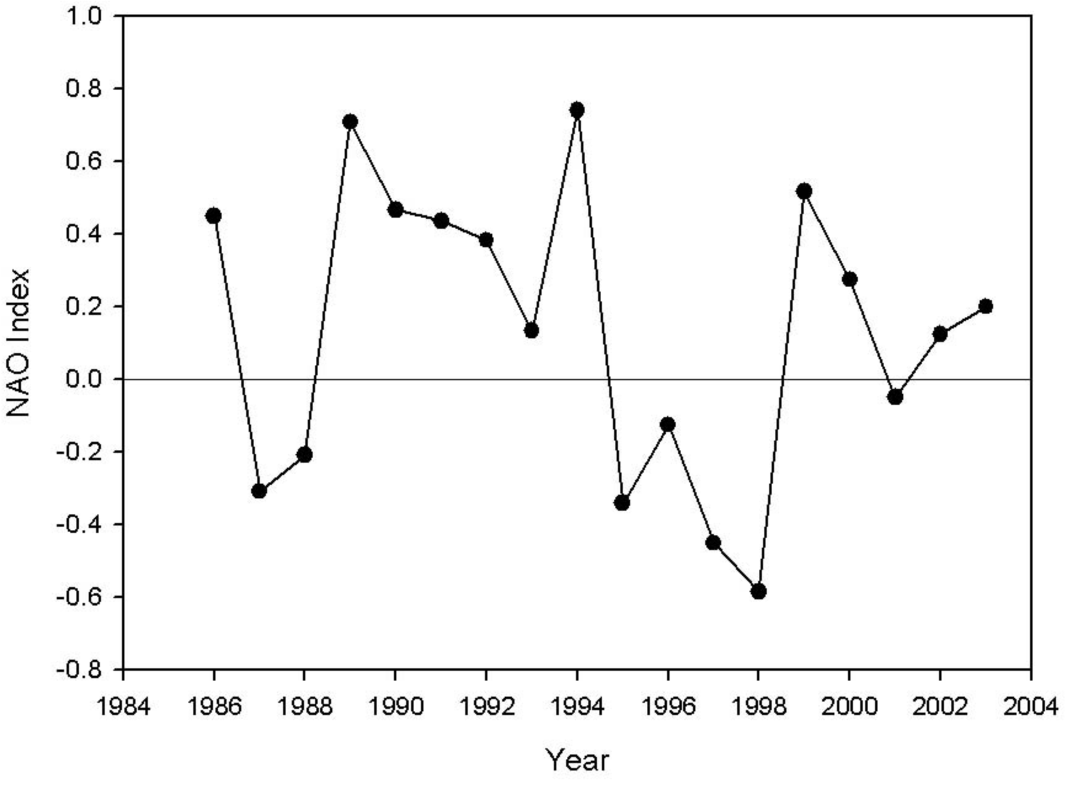

Figure 1.3. Mean annual NOA index

1.3 Acidity

Acidity in precipitation is not a conserved quantity and is controlled by the presence of other ions in solution. While the initial focus of the work on acid deposition was acidity per se, the sources of the acidity are of course the primary scientific focus, these being non-marine SO_4 and NO_3 and for some areas of the UK non marine Cl. However, the acidity in UK precipitation has declined dramatically over the monitoring period, at most of the monitoring stations. Considering the 28 sites with 14 years or more, 22 show a statistically significant reduction in acidity over the monitoring period, varying from -4 ueq l^{-1} yr^{-1} in the East Midlands of England to –0.5 ueq l^{-1} yr^{-1} in Wales. These reductions in acidity in the most polluted regions of Eastern England vary from 40% to 60% from the values of the late 1980s. In the high rainfall regions of Wales, Cumbria and Western Scotland the absolute reductions in acidity are much smaller, but at many sites, there is still a statistically significant decline in acidity. The 6 sites with more than 14 year records which show no significant change are located in two areas of the UK, first the remote regions of west and northern Scotland, which are remote from the major source areas and were never regions of very large wet deposition of acidity, and secondly the South West of and South East coasts of England, (Barcombe Mills, Yarner Wood and Goonhilly) where shipping sources of acidity have continued to contribute significant sources of acidity. In these areas of southern and especially SW England, the contribution to wet deposition from shipping is steadily increasing as the terrestrial sources decline.

The mean acidity in the network over 1986 to 2002 is shown in Fig 1.4., with the trend in the averaged data clearly evident with a decline in ‘UK average rainfall acidity’ of ueq l^{-1} yr^{-1}. By the year 2000 acidity had halved over the country, with larger reductions in the most polluted regions.. The regional variability is interesting and shows for the sites in Group 1, a decline in acidity from ~50 to ~25 ueq l^{-1} yr^{-1} and is the region in the UK in which has changed most during the monitoring period. There were concerns in earlier reports on rainfall acidity trends that in parts of Western Britain, no reduction in acidity was evident. The longer data series is now revealing reductions in acidity in Wales, and the trends are generally clearer in western Britain, but there remain sites and areas of the country where despite very large reductions in emissions at the national scale, the acidity in precipitation has not declined.

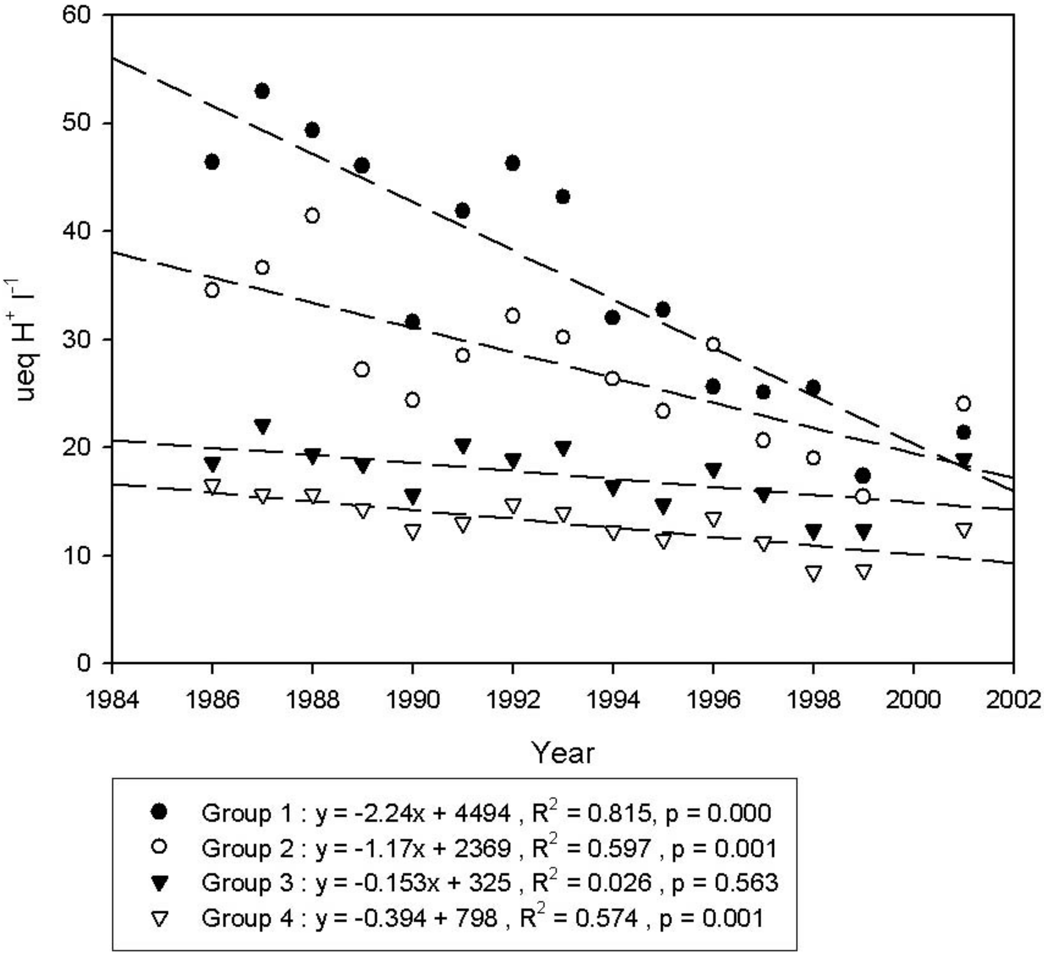

Figure 1.4. Trends of H in precipitation (sites grouped as in Table 1.1)

1.4 Marine derived ions Na, Cl, Mg

The oceanic climate of the UK is a characteristic feature of both the physical and chemical climate of the country, and precipitation chemistry, especially close to the coast is often dominated by marine derived ions and SO_4, NO_3, and Mg in particular. The trends in Na over the monitoring period (Fig 1.5.) are non significant at most sites, but it is notable that three of the sites, all in central England or in the East Midlands show a significant decline in Na over the 16 years of about 2 ueq l^{-1} yr^{-1}, which is a significant fraction of the concentration at these locations. As the decline is significant statistically at a few sites where the marine influence is small, an explanation is called for. At most of the remaining sites the changes in Na are negative, and while non-significant statistically, it is interesting that for most of the inland sites, the trend is of a similar magnitude, 1 to 2 ueq l^{-1} yr^{-1}.

A possible cause is a reduction in the application of road salt, which is resuspended by vehicles and may have declined in the recent, mild and wet winters. However, so far it has been difficult to find supporting data to check the application of road salt on UK roads during the last 20 years.

At most of the remaining sites the changes in Na are negative, and while non-significant statistically, it is interesting that for most of the inland sites, the trend is of a similar magnitude, 1 to 2 ueq l^{-1} yr^{-1}.

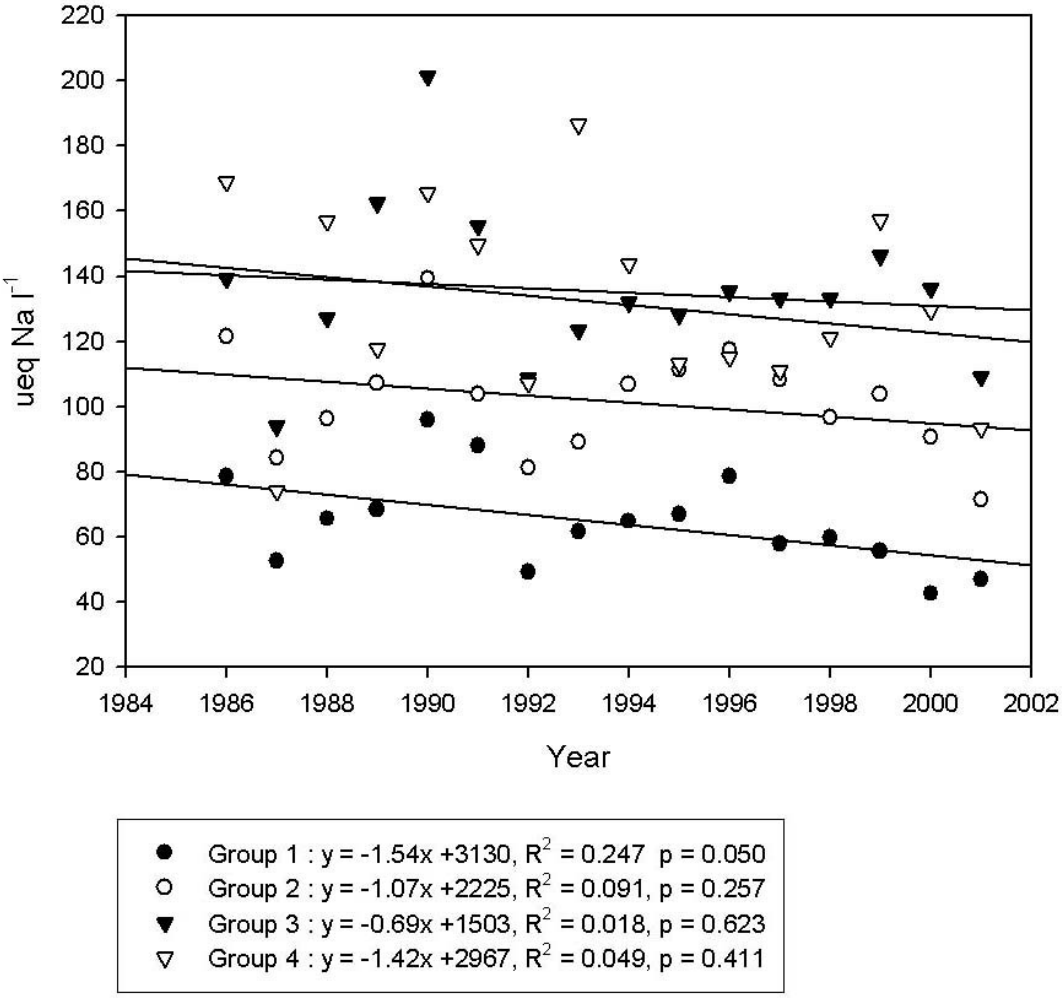

Figure 1.5. Trends in Na in precipitation (sites grouped as in Table 1.1)

For Cl the story is more complex, due to additional sources of Cl to the atmosphere from the Cl in coal and from combustion of Cl containing waste (Cape and Lightowlers 1988). Considering the total Cl in precipitation, (Fig 1.6.), the data appears very similar to Na, confirming the importance of marine sources for these ions in UK precipitation. Again there is a significant decline in concentration in the Group 1 sites in central England, but in this case the magnitude of the decline is larger than that for Na because the non-marine Cl from coal combustion has also declined appreciably during this period. The non-marine Cl concentrations show a very large decline, from about 20 ueq l^{-1} in 1986 to current values close to 5 ueq l^{-1} in the English midlands and the area in which statistically significant declines in non-marine Cl are observed include both group 1 and group 2 sites, therefore including almost all of southern England, and extending into eastern Scotland.

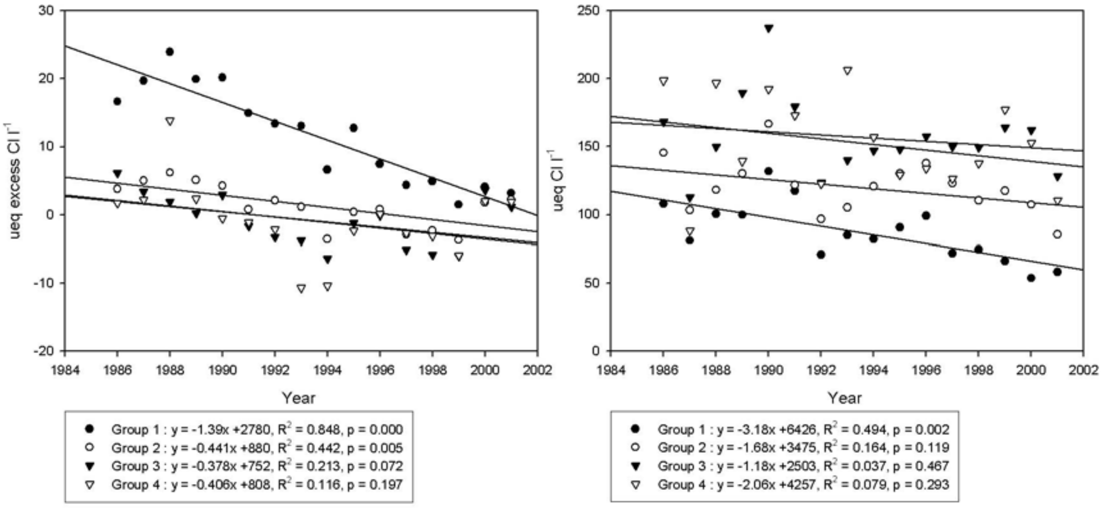

Figure 1.6. Trends of excess Cl and total Cl in precipitation (sites grouped as in Table1.1)

1.5 Non-marine SO$_4^{2-}$

The major source of acidity in precipitation during the 1970s and 1980s was SO$_4^{2-}$ and this was the ion on which most attention was focussed. Trends in SO$_4^{2-}$ in UK precipitation were clear at Group1 and 2 sites in the NEGTAP report, considering data upto 1997, but west coast sites showed non-significant trends, in part due to shipping emissions. With the longer time series, the trends SO$_4^{2-}$ are now statistically significant in all the groups (Fig 1.7.). The magnitude of the decline is notable, amounting to 50% at group 1 sites and even at the remote sites in Group 4, the decline approaches 50% over the 16-year monitoring period. The data for the last 4 years has clearly made an appreciable difference to the countrywide picture and show a recovery of the precipitation chemistry, at least in the respect of SO$_4^{2-}$, to values not recorded in the UK since 1950s (Stevenson et al 1968). There are earlier data, from the work of Smith (1872), and Laws and Gilbert (1919), but there was no UK network before 1950 and the protocols for collection and analysis are not described in sufficient detail to be confident in making comparisons with current data.

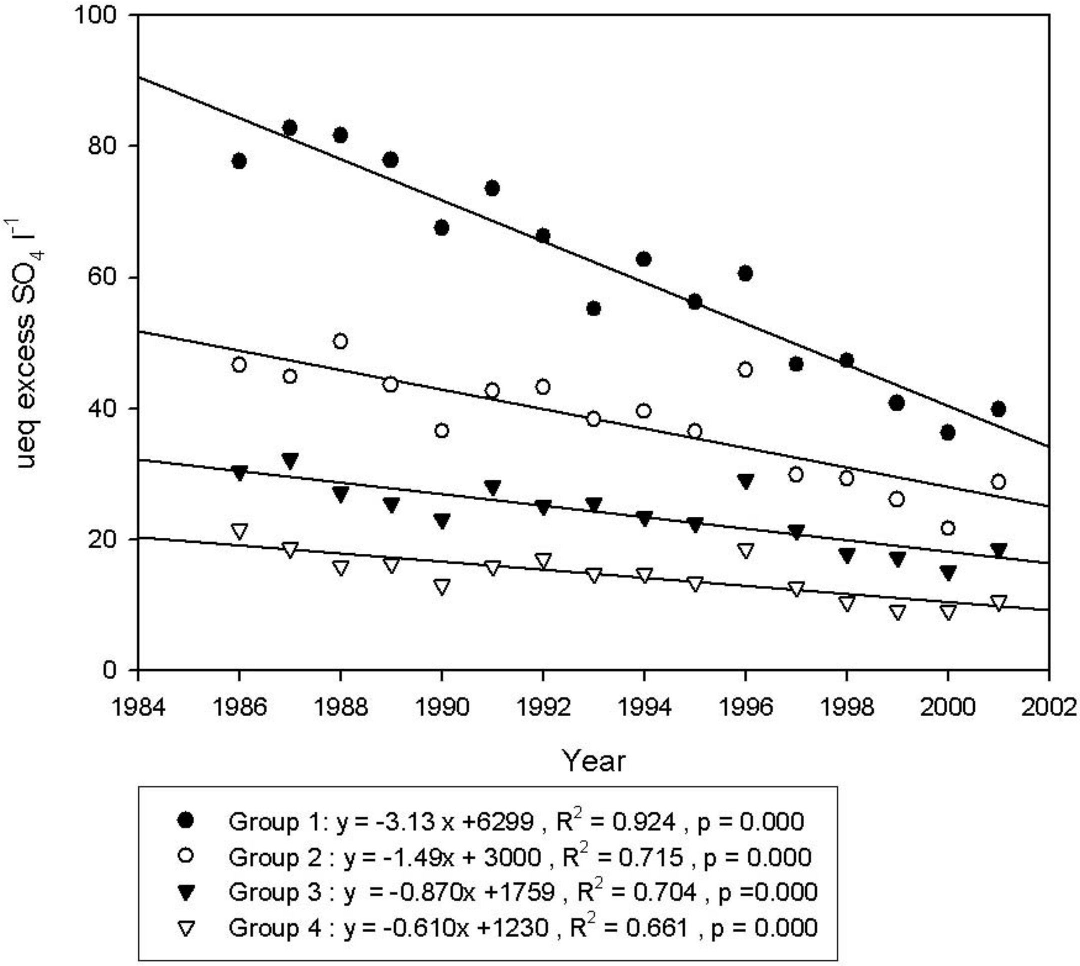

Figure 1.7. Trends in excess SO_4 in precipitation (sites grouped as in Table 1.1.)

1.6 NO_3

Changes in UK concentrations of NO_3 in precipitation are shown in Fig 1.8.. The data show a reduction in concentration over substantial areas of England. The trend at individual sites is statistically significant at the sites in the east and south of England and Scotland, and at one site in the west coast of Scotland (Polloch).The grouped data show a significant trend only in Group 1, amounting to a reduction in NO_3 of about 10% in the 16 year record and compares with a reduction in emissions of NO_x in the UK and the EU of 50% and 35% respectively over the monitoring period. Concentrations of NO_3, from the oxidation of NO_x in the atmosphere are not complicated by significant marine sources, and would be expected to respond to changes in the regional (European) emissions unless there is an additional contributor to the NO_x budget over the UK from non-European sources, or, that the reduction in official emissions has been overestimated.

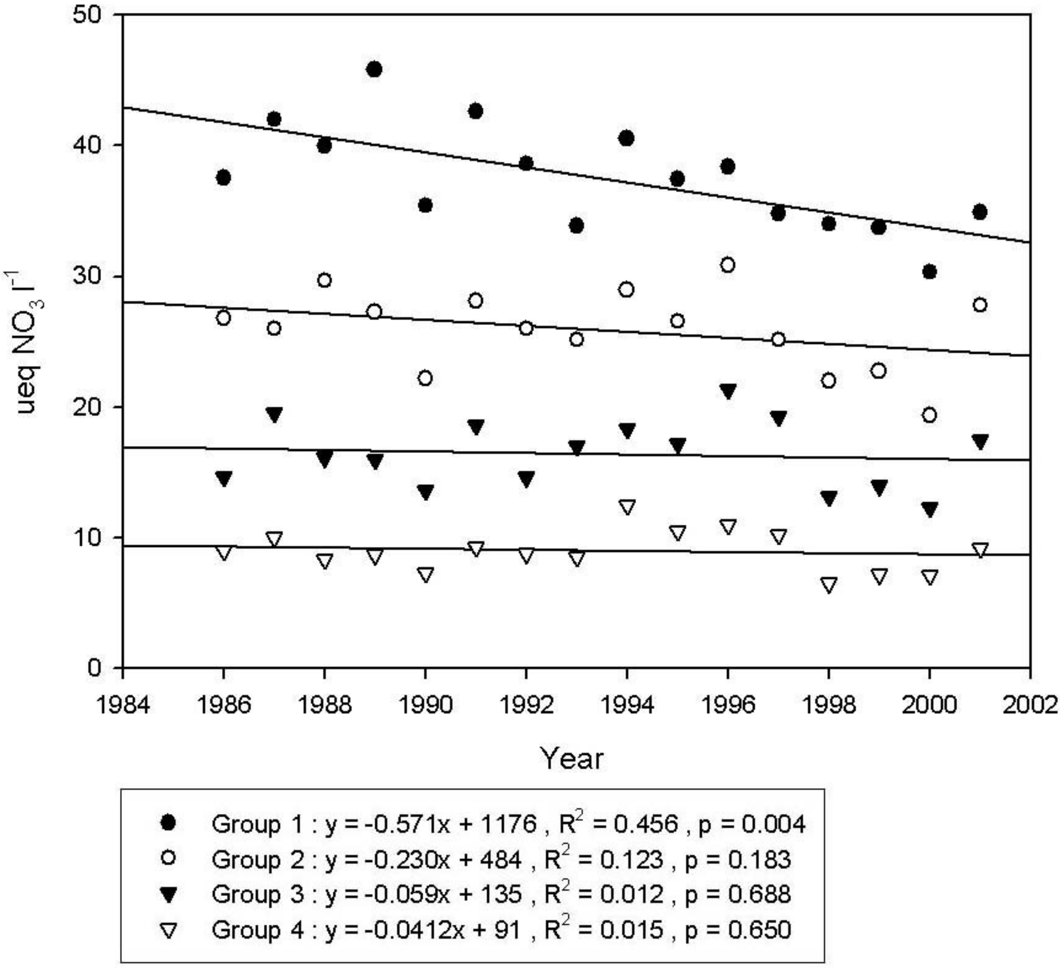

Figure 1.8. Trends of NO_3 in precipitation (sites grouped as in Table 1.1).

It is notable in the data, that concentrations decline at 75% of the sites with at least 15 years data, and the sites showing an increase are all non-significant and are all relatively remote sites in the west and/or north of the UK. However, the much smaller decline in NO_3 concentration than that in emissions throughout Europe is an important feature of the data and merits an explantion.

1.7 NH_4

Along with SO_4 and NO_3, the other major ion in precipitation from anthropogenic activity is NH_4. In the early days of the monitoring network, concentrations of NH_4 were among the largest of the three and especially in the source regions of the English Midlands, NH_4 concentrations were generally larger than NO_3. The main sources are agricultural, with intensive production of livestock and beef and dairy cattle in particular being the largest contributors. The data (Fig 1.9.) show a decline in NH_4 concentration at 6 of the long-term sites, and as these are all in Group 1, this group shows a statistically significant decline, amounting to about 20% over the 16 years. Many sites show non-significant declines but most changes over the monitoring period are negative rather than positive. Given the very large decline in SO_4 concentrations the reduction in acidic aerosol concentrations with which it was associated, the scavenging of NH_4 would be expected to change, and, in particular an increase in travel distance of NH_4 and a gradual change in the partitioning of NH_3/NH_4. Emissions of NH_3 have declined by about 12 % since 1990, and the larger reduction in NH_4 concentration are broadly consistent with the change expected through the combination of the emission reduction and the changing atmospheric sinks in the source region.

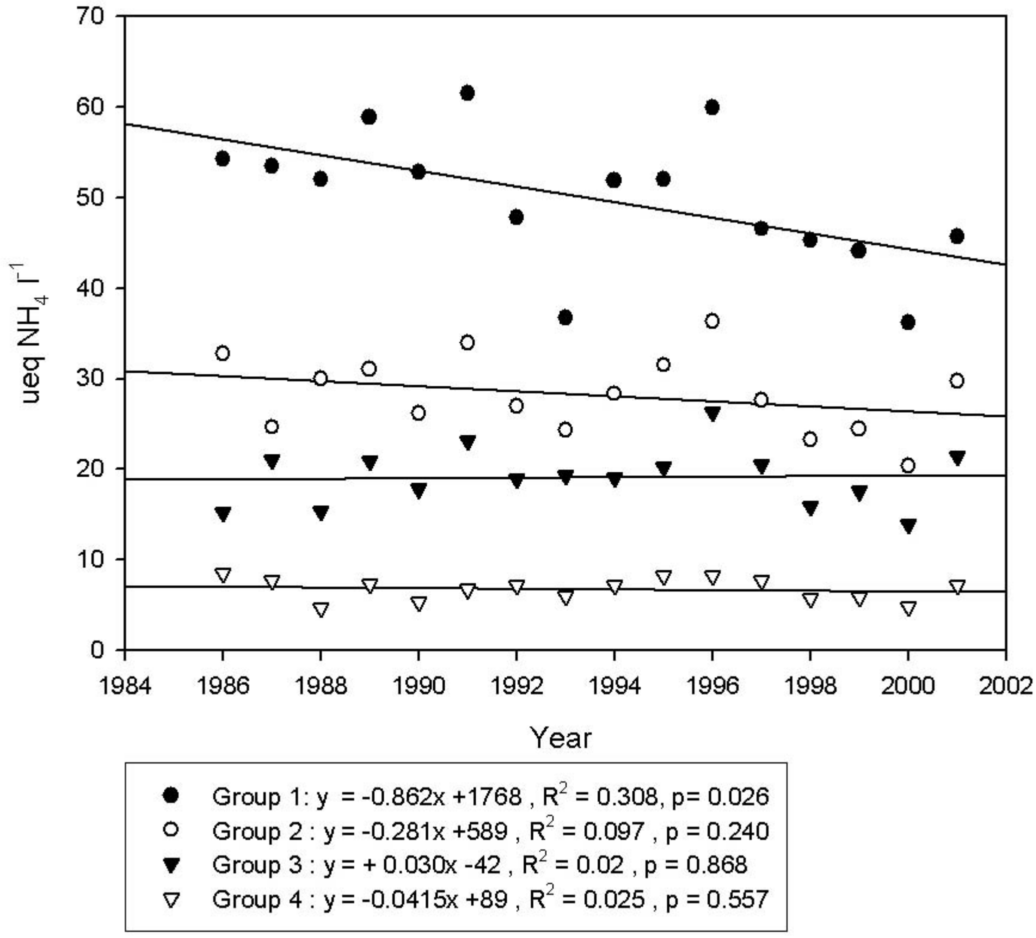

Figure 1.9. Trends of NH_4 in precipitation (sites grouped as in Table 1.1.)

1.8 Ca, Mg

The base cations are generally minor contributors to the ionic strength of precipitation, but are important in the overall acid deposition story as they contribute acid neutralizing ions to the surface and as such are very important contributors to the recovery of fresh waters in catchments with very slow weathering soil and parent mineralogies.

The data for these ions show a clear decline over the monitoring period, but the record is limited to the period 1986 to 1991 and 2000 to 2001.The missing years have been deleted due to analytical problems. However, it is clear that concentrations have declined substantially at many of the sites in the English Midlands, with rates of change between 1 and 2 ueq l^{-1}, amounting to a reduction of nearly 50% at the sites with largest concentrations of Ca. The cause of the decline is most likely a consequence of reduced emissions of Ca from combustion plant.

Acid Deposition Processes: SO_2 monitoring

EPG 1/3/166

Garry Hayman, Keith Vincent, Ron Smith, David Fowler and Robert Storeton-West

Centre for Ecology and Hydrology
(Edinburgh Research Station)
Bush Estate, Penicuik,
Midlothian, EH26 0QB, UK.

netcen
AEA Technology
E5 Culham, Abingdon
Oxon., OX14 3ED, UK

SO_2 concentration monitoring

- The monitoring network now operates with filter pack sampling, which has lower a detection threshold than the bubbler and appears satisfactory for the network.
- Problems of breakthrough in the early phase of the new method have been eliminated and the network is now operating well.
- SO_2 concentrations throughout the UK have declined since 1980, and 1986, the average concentration has declined from about 2 ppb to about 0.2 ppb in 2001.

2. THE RURAL SO_2 MONITORING NETWORK

2.1. Introduction

One of the objectives of the present project is to quantify *inter alia* the deposition budgets of sulphur for the United Kingdom so that the acidifying effects of sulphur deposition on freshwater, soils and vegetation can be assessed. This requires the determination of sulphur deposition from both its wet and dry deposition pathways. The dry deposition budget is derived by combining a sulphur dioxide (SO_2) concentration field with estimated deposition velocities. As part of this project, AEA Technology manages and operates the UK Rural Sulphur Dioxide Monitoring Network to determine monthly and annually-averaged concentrations of SO_2, which are subsequently used to produce concentration fields for the UK.

This section provides an overview of the monitoring network, the samplers used and the measurements made. Reports containing more details of the monitoring programme and measurements made in the calendar years 1997-2001 have been prepared [Hasler *et al.,* 2001; Hayman *et al.*, 2001a, 2001b, 2003b, 2003c] and are available from Defra's Air Quality Archive site (http://www.airquality.co.uk/archive/index.php).

In recent years, the sulphur dioxide concentrations measured at some of the sites in the monitoring networks (*i.e.*, the UK Acid Deposition Monitoring networks and the UK Rural Sulphur Dioxide Monitoring network) have been at or below the limit of detection (LOD) of the current hydrogen peroxide bubbler method. This will make it more difficult to determine reliable trends and could compromise the application of the monitoring data, for example, in identifying the cause of the non-linear response of ambient concentrations to change in emissions at such sites. A change in sampling method was required which would provide a lower LOD while retaining data integrity and consistency.

An intercomparison exercise was undertaken at the Auchencorth Moss site between September 1998 and May 1999 to evaluate potential replacement methods. A summary of the intercomparison exercise and the results obtained were given in the 1999 Data Report [Hayman *et al.*, 2001b]. A more detailed description is provided in Hasler *et al.* [2000]. On the basis of the intercomparison exercise, the choice of methods to replace the bubbler method was limited to the denuder or the filter pack methods on the grounds of cost, improved sensitivity, method robustness, ease of operation and the quality of the measurements.

The filter pack method was preferred for practical reasons and the new samplers were introduced into the monitoring network from April 2001. At five sites, both the bubbler and filter-pack sampler have been operated side-by-side. A summary of the relative performances of the two instruments is included in this report.

2.2. Network and Sampling Details

2.2.1. THE MONITORING SITES

At the commencement of the project in November 2000, the Rural Sulphur Dioxide monitoring network comprised 31 sites at which concentrations of SO_2 were measured on a weekly basis and one site (Bush) at which daily measurements were made. There are a further 8 sites in the Acid Deposition Monitoring Network at which daily measurements are also made. Siting criteria and individual site assessment are given in Downing and Campbell [1995]. In general, the monitoring sites are located in rural areas which are largely unaffected by local domestic and industrial sources but which are representative of the surrounding region.

The measurements made in the Rural Sulphur Dioxide Monitoring Network are however significantly enhanced by including data which have been obtained in other SO_2 monitoring networks. These include:

(i) the continuous monitoring sites operated by the power generating companies. The sites are located in Yorkshire, Nottinghamshire and the Thames Estuary;

(ii) five of the continuous monitoring sites from the Defra's Automatic Urban and Rural Network;

(iii) the two continuous monitoring sites operated by CEH Edinburgh at Sutton Bonington and Auchencorth Moss.

The location of the sampling sites is shown in Figure 2.1.

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2.2.2. SITE CHANGES WITHIN THE NETWORK BETWEEN 2000 AND 2003

Following the retendering of the contract in 2000, the sites at Bylchau (site 5334) and Crai (site 5335), which were operated and managed under a separate contract let by the National Assembly of Wales, were incorporated into the Rural SO_2 Monitoring programme. During the contract, a number of sites were relocated to nearby locations because of restrictions on access (Brockhill, 5301) or changed use of the buildings housing the samplers (Cam Forest, 5329). Other sites were closed and new sites opened. Table 2.1 list the site changes that have occurred during the present project.

Table 2.1 - Summary of Site Changes in the Network between 2000 and 2003.

Site	**Comment**
5301 – Brockhill	Site closed on 28/2/2002 as access restrictions precluded sampling during 2001; sampler moved to Drayton in 2002
5306 – Cardington	Close to site at Husborne Crawley; Site closed on 30/1/2002 and sampler moved to Church Fenton
5315 – Ratcliffe	Site closed on 4/12/2001 and effectively replaced with that at Sutton Bonington.

5329 – Cam Forest	Sampler moved to Formoyle on 22/11/2001 as changed use of building housing the sampler at Cam Forest
5340 – Garrary	Sampler moved to Benniguinea in August 1999
5343 – Benniguinea	Replaced Garrary site; sampling commenced in August 1999
5344 – Sutton Bonington	Site selected as a sampler intercomparison site and sampling commenced on 8/5/2001.
5345 – Formoyle	Replaced Cam Forest site; sampling commenced on 22/11/2001.
5346 – Drayton	Replaced Brockhill site; sampling commenced on 28/2/2002.
5347 – Church Fenton	New site established on 16/10/2002 close to the major power stations in Yorkshire

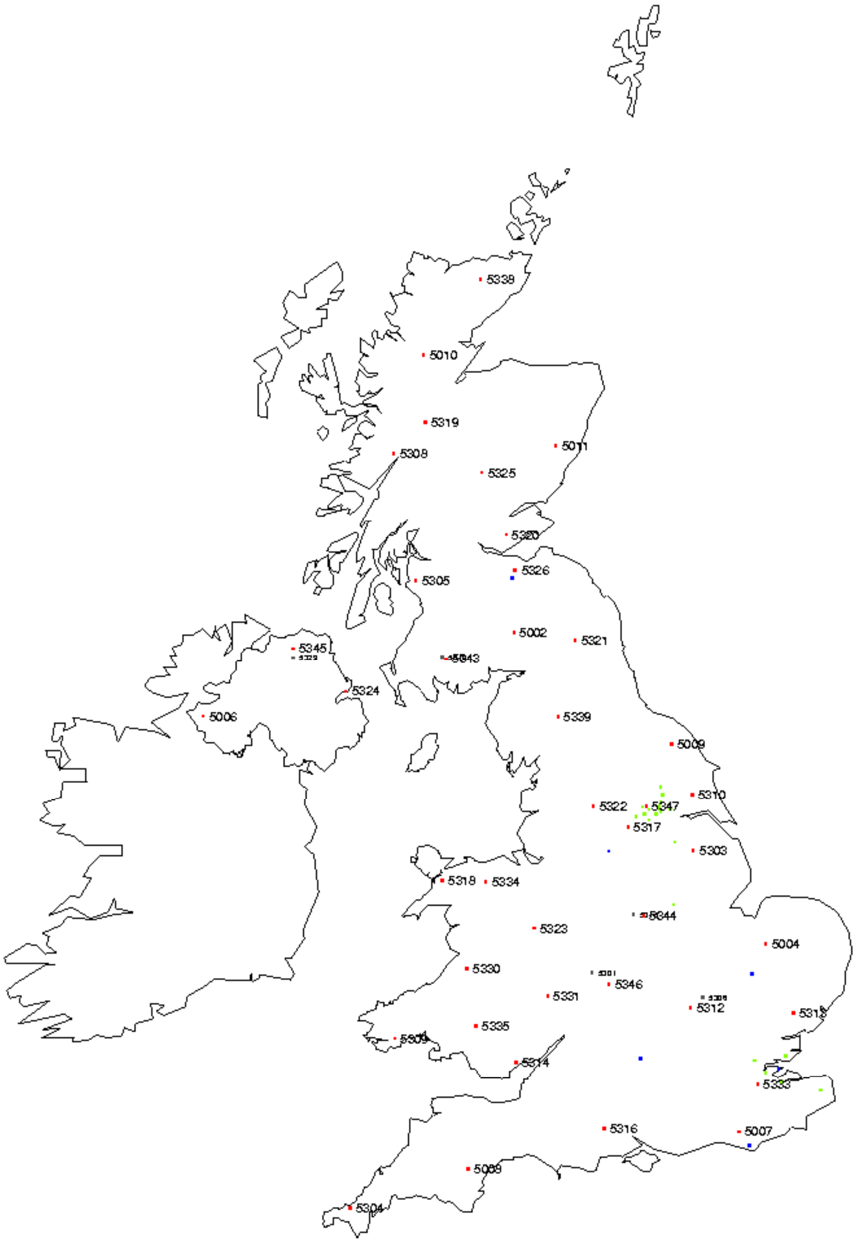

Figure 2.1 - Location of the Sites Used to Monitor and to Map SO_2 Concentrations (red - network sites; black – closed sites; green – JEP sites; blue –other rural SO_2 sites).

2.2.3. THE SAMPLING TECHNIQUE

The Hydrogen Peroxide Bubbler Technique

At the start of the contract, the concentration measurements were made using the hydrogen peroxide bubbler technique [Downing and Campbell, 1995]. In this sampling method, air is drawn through a filter to remove any particulate matter (including particulate sulphate) and then through a hydrogen peroxide solution, where sulphur dioxide is absorbed and oxidised to sulphate. The resulting sulphate concentration in the solution is determined by ion chromatography. The ambient concentration of sulphur dioxide is derived from the concentration of sulphate determined analytically and the volumes of (a) the air drawn through the bubbler during the sampling period and (b) the H_2O_2 solution.

There are three versions of the bubbler used in the Rural SO_2 and Acid Deposition monitoring networks:

- an 8-port bubbler is used at nine sites and analysis of each daily sample is undertaken to give a daily measurement;
- an 8-port bubbler is used at 25 sites. The individual samples are bulked and a single analysis is undertaken to give a weekly measurement;
- a single-port bubbler is used at 6 sites. A single sample is collected and analysed to give a weekly measurement.

The bubbler method is an EMEP recommended method [EMEP, 1996].

The Filter Pack Sampler

The Filter Pack sampler consists of two filters in series which are enclosed in an airtight holder. Air is drawn through the filter pack and sulphate aerosol particles are removed on the first filter. Sulphur dioxide is absorbed by the second filter, which has been previously washed with potassium carbonate and then impregnated with a glycerol/potassium hydroxide solution. It is quantitatively converted to solid potassium sulphite by reaction with the potassium hydroxide and oxidising species in the air convert the sulphite to sulphate during sampling. The sulphate on the exposed impregnated filter is extracted using water. The sulphate concentration in the solution is determined using ion chromatography and this is converted into a gas-phase concentration of sulphur dioxide.

This is also an EMEP recommended method [EMEP, 1996].

2.2.4. EQUIPMENT MAINTENANCE

Regular equipment maintenance is needed to maximise data capture and sample quality. The sites within the network are visited annually to ensure all equipment is operated within acceptable working limits.

The bubbler and filter-pack units are based on a simple design with few moving parts. However, the motors within the sampling pumps occasionally fail. Consequently, the airflows at all sites are routinely monitored so that failing pumps can be identified and replaced before complete failure occurs. The sampling flowrate for the bubbler is maintained between 2 and 4 m^3 per day. The filter-pack uses a higher flow rate of 30 m^3 per day.

To ensure airflows are recorded accurately the airflow meters are calibrated at least once a year against a certified wet gas meter (standard meter). The accepted tolerance for bubbler meters is where their measured air volume is within 3% of that measured by the standard meter. If meters are found to fall outside this criteria they are withdrawn from use and replaced.

2.2.5. SENSITIVITY OF THE SAMPLING TECHNIQUES

The same ion chromatographs are used to determine the concentration of sulphate from both samplers. The instrument has an analytical limit of detection of 0.01 mg [SO_4^{2-} as S] per litre of solution. For the volumes of H_2O_2 solution (400 cm^3) and air flow rates (2-4 m^3 per day) used in the bubbler method, this implies that the limit of detection for ambient SO_2 concentrations will vary between 0.15-0.30 µg SO_2 as S m^{-3} (0.1-0.2 ppb SO_2), depending on the actual air flow rate reported. For the filter-pack sampler, although the analytical limit of detection remains unchanged, significantly lower concentrations can be measured as higher air flow rates (210 m^3 over a fortnight sampling period = 15 m^3 per day) and a smaller extraction volume (25 cm^3) are used. The filter-pack limit of detection for ambient SO_2 concentrations is 0.0012 µg SO_2 as S m^{-3} or 0.0009 ppb SO_2.

2.2.6. DATA CAPTURE

Annual and monthly mean concentrations are only calculated if the data capture exceeds 75%. There are a number of reasons why the concentrations cannot be determined for individual samples. These include:

Frequent	• The electricity supply is interrupted and the sample collected is not representative of that week's concentration. • A failure of the pump/meter/bubbler occurs.
Occasional	• The sampler is switched off by the site operator when the site operator is unavailable. • A long sampling period occurs when the site operator is unavailable (2 weeks plus usually) which because of the lack of fluid reservoir is not representative of that sampling period (H_2O_2 falls below dreschel stems in bottles). • An error or mix-up is made by the site operator. • The sample solution in the bubbler partially or completely leaks during transit because the sample container lids were not secured effectively. The total sample volume is unknown and the concentration in air can not then be calculated. • The parcel is lost during transit.
Rare	• The sample is lost during analysis or sample registration. • Vandalism at the monitoring site may cause the sample to be lost.

There were specific instances when sampling was affected over an extended period at certain sites:

- In 1998, there were recurrent problems at Pitlochry (5325) with failing pumps which caused low air flow rates. The samples collected in the second half of 1998 were discarded and no annual mean concentration could be calculated. At the Fort Augustus site (5319), there were difficulties with the sample changeover in July and August, which resulted in these samples being discarded. Despite this, the overall data capture for the year was sufficient to allow an annual mean concentration to be calculated.
- In 1999, a recurrent problem with a fluctuating power supply at the Fort Augustus site (site code 5319) affected the performance of the pump and resulted in frequent loss of data between January and September. The low data capture precluded the determination of an annual mean concentration. The pressure drop on the inlet following the introduction of a new fan at the Bush site (site code 5326) caused intermittent suck back

of the bubbler solution. No data were collected between the end of July and the middle of September when the problem was resolved.

- During 2000, there were no sites where the sampling programme was affected for extended periods, although equipment failure led to the loss of samples over periods of up to several weeks at certain sites.
- Access restriction to the Brockhill site prevented sample collection throughout much of 2001. As a result, this site was relocated to Drayton in early 2002.

2.3. Comparison of the Bubbler and Filter-pack Samplers

2.3.1. OVERVIEW

In recent years, the sulphur dioxide concentrations measured at some of the sites in the monitoring networks have been at or below the limit of detection (LOD) of the bubbler method. A change in sampling method was required to provide a lower LOD while retaining data integrity and consistency. Following the intercomparison exercise undertaken at the Auchencorth Moss site near Edinburgh between September 1998 and May 1999, the filter-pack method was selected to replace the hydrogen peroxide bubbler method. The filter-pack sampler introduced into the monitoring network from April 2001.

At five sites, with very different sulphur dioxide environments, both the bubbler and filter-pack sampler have been operated side-by-side to compare the performance of the two samplers and hence to define the transfer function. The five sites selected are shown in Table 2.2, together with the periods when the two samplers were operated side-by-side.

Table 2.2 - *Overlap Periods of the Bubbler and Filter-pack Samplers at the 5 Selected Sites.*

Site	Overlap Period(s)
5006 - Lough Navar	24/04/2001 - 05/11/2001 29/01/2002 - present
5010 – Strathvaich Dam	19/06/2001 – 31/12/2001
5326 – Bush	23/05/2001 – present
5330 – Cwmystwyth	26/04/2001 - present
5344 – Sutton Bonington	15/05/2001 - 29/12/2001 30/01/2002 - 03/07/2002

Lough Navar and Strathvaich Dam are remote sites where very low SO_2 concentrations are observed. Bush and Cwmystwyth are intermediate sites with annual mean concentrations of typically 1 ppb. Sutton Bonington is a high concentration site, not far from a major source of SO_2 at Ratcliffe on Soar.

2.3.2. RELATIVE PERFORMANCE OF THE BUBBLER AND FILTER-PACK SAMPLERS

The daily bubbler and fortnightly filter-pack measurements made at Bush between 2001 and 2003 are shown in Figure 2.2. At this site, SO_2 concentrations are also made using an automatic UV-F analyser. Figure 2.2 also includes the UV-F and daily bubbler measurements averaged over the same sampling periods as those of the filter-pack measurements. The agreement between the three samplers was good, both qualitatively and quantitatively.

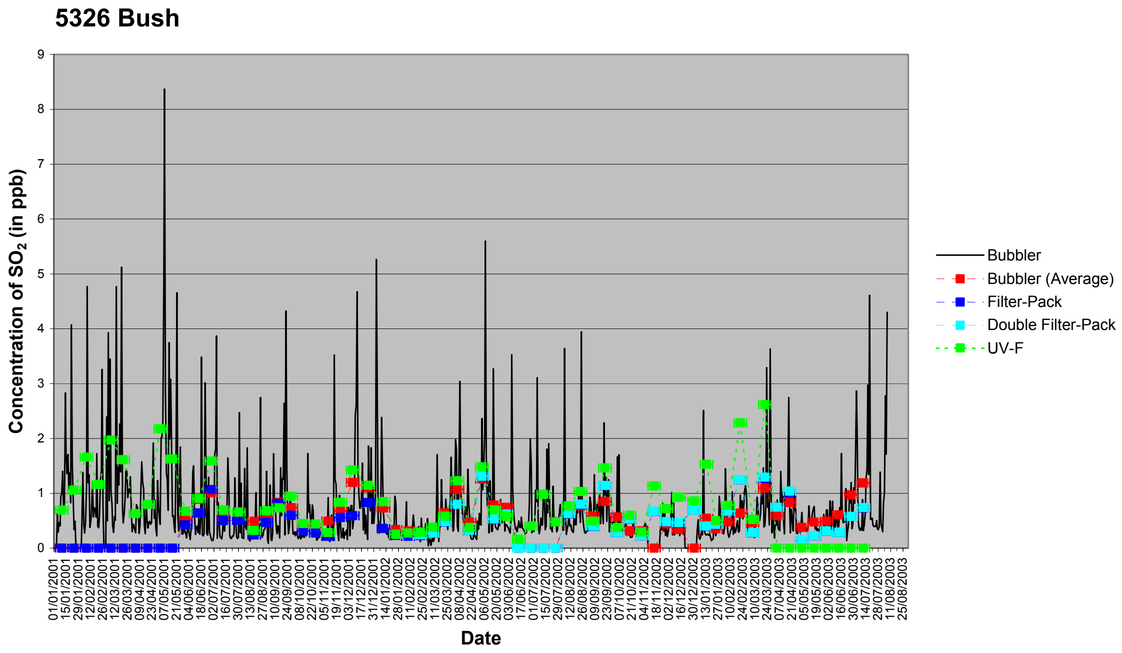

Figure 2.2 - *Comparison of the Bubbler, Filter-pack and UV-F Measurements made at Bush between 2001 and 2003.*

In Figure 2.3, the bubbler and filter-pack measurements are compared at the other four overlap sites (Lough Navar, Strathvaich Dam, Cwmystwyth and Sutton Bonington). At the low concentrations sites of Lough Navar and Strathvaich Dam, there does not appear to be any evidence that the bubbler measurements are at or below the limit of detection of the technique. Indeed, the measurements suggest that there is an offset between the two samplers.

From Spring 2002, there was a significant change in the relative performances of the two samplers. This is most clearly seen in the measurements made at Lough Navar and Cwmystwyth where the filter-pack sampler reported much lower concentrations. As will be seen subsequently, this was traced to a change in the performance of the bubbler.

An unweighted linear regression analysis was undertaken of valid pairs of filter-pack and bubbler measurements at each site, as shown in Figure 2.4. All the measurements from mid 2002 onwards have been excluded. The resulting regression coefficients are summarised in Table 2.3. The coefficient of determination is greater than 0.75 at all the sites. The valid measurements from all 5 sites were then combined into a single regression analysis, as shown in the bottom right-hand panel of Figure 2.4 and these regression coefficients are also summarised in Table 2.3.

$$[SO_2]\text{ filter-pack} = 1.049\ [SO_2]\text{ bubbler} - 0.108$$

The analysis indicates that there is (a) an almost 1:1 relationship between the two sampler measurements and (b) that the filter-pack sampler underreads by ~0.1 ppb. This results almost replicates that obtained previously during the Auchencorth Moss intercomparison study.

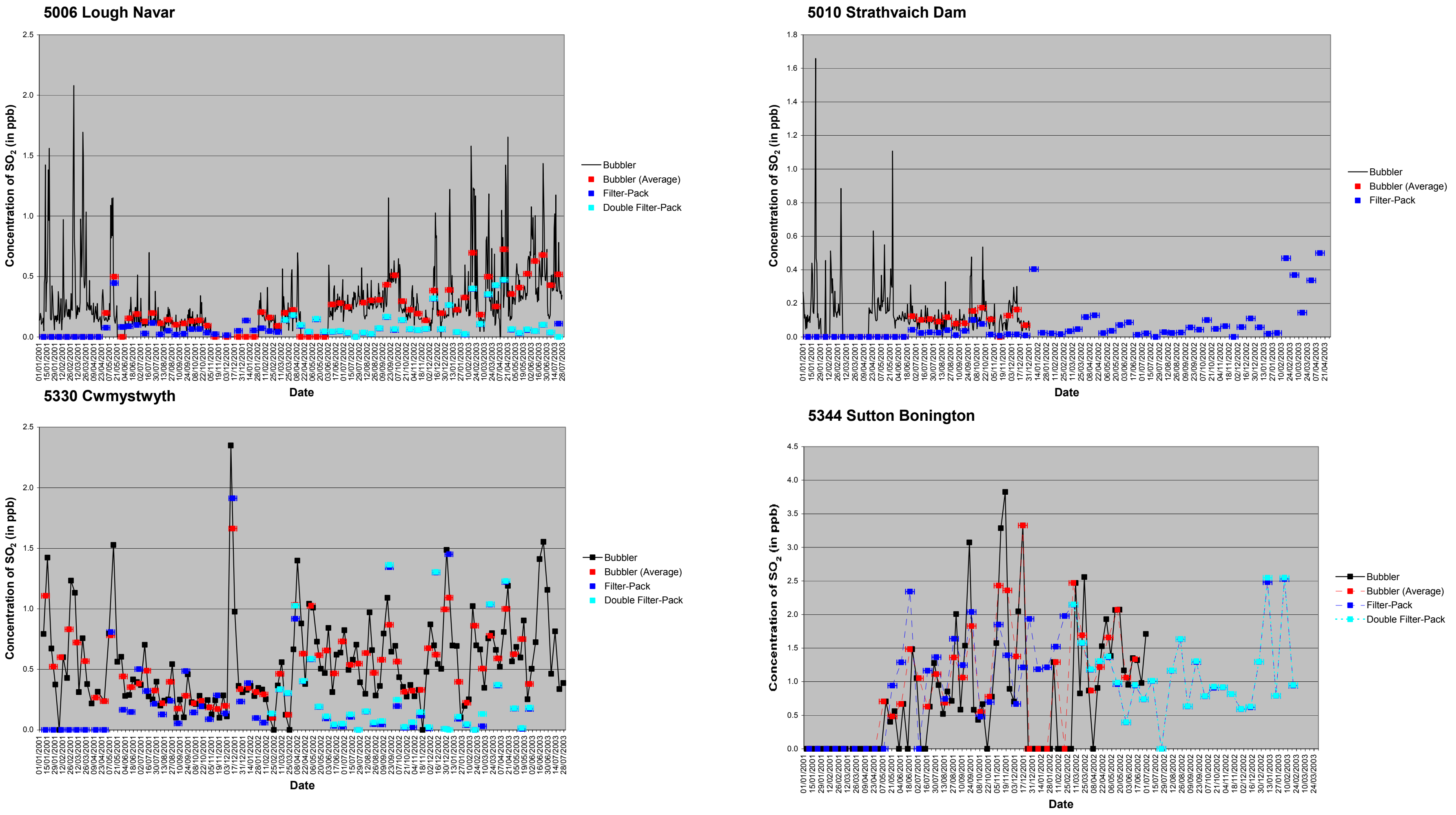

Figure 2.3 - Comparison of the Bubbler and Filter-pack Measurements made at the Other Overlap Sites between 2001 and 2003

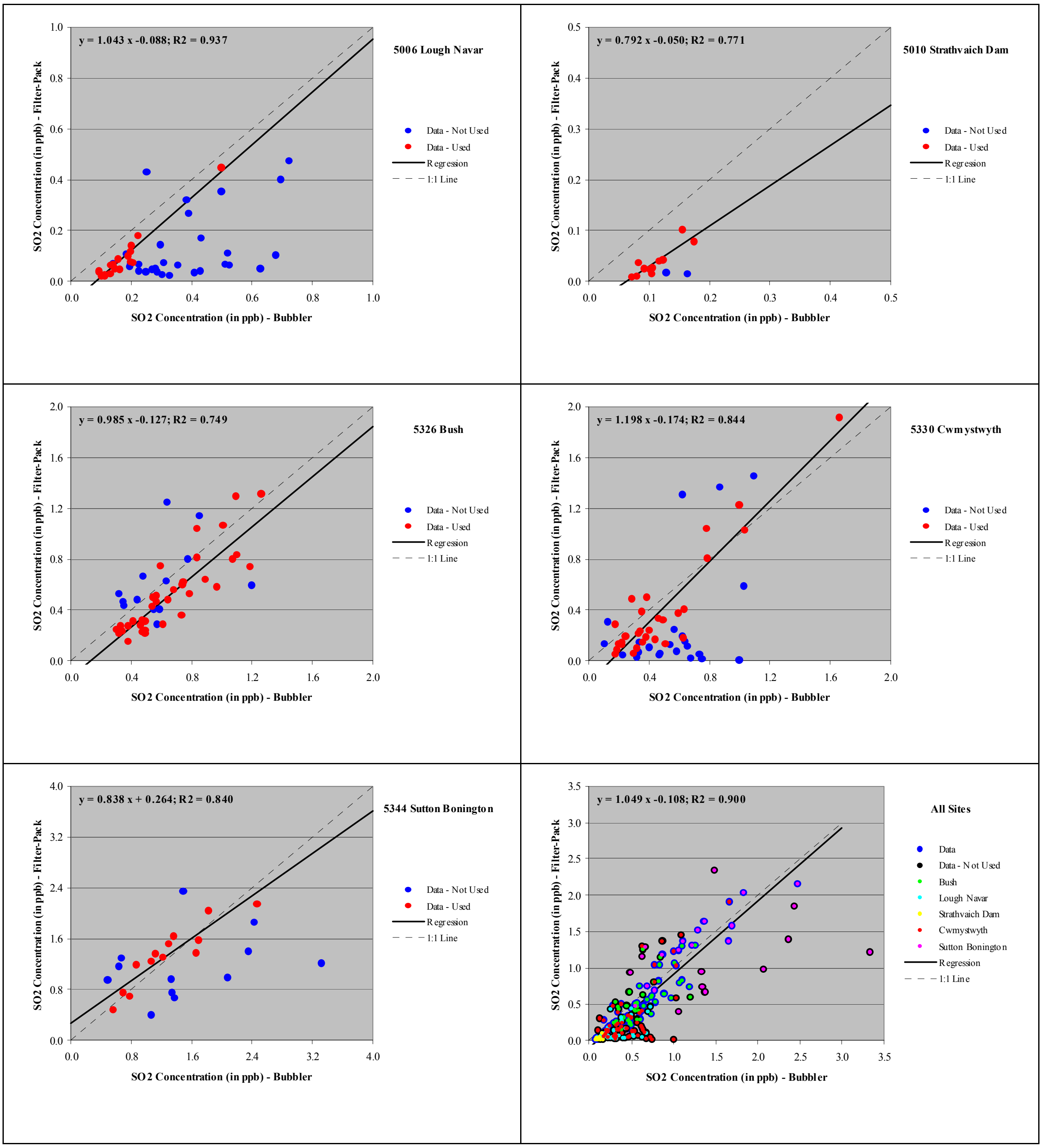

Figure 2.4 - *Unweighted Linear Regression Analyses of the Valid Filter-pack and Bubbler Measurements at Each of the Overlap Sites and All Sites combined.*

Table 2.3 - *Summary of the Regression Analysis of the Filter-pack vs Bubbler Measurements.*

Site	# Datapoints Used	# Datapoints Not Used	Slope	Intercept	Coefficient of Determination
5006 Lough Navar	18	29	1.043	-0.088	0.937
5010 Strathvaich Dam	11	2	0.792	-0.050	0.771

5326 Bush	35	14	0.985	-0.127	0.749
5330 Cwmystwyth	29	23	1.198	-0.174	0.844
5344 Sutton Bonington	13	12	0.838	0.264	0.840
All Sites	**106**	**80**	**1.049**	**-0.108**	**0.900**
Auchencorth Moss	13	-	0.938	-0.135	0.688

A possible explanation for the underread of the filter-pack sampler could be incomplete capture of SO_2 by the single impregnated filter paper. This was eliminated as the addition and subsequent analysis of a second impregnated filter showed that there was little if any breakthrough. Another possible explanation could be the capture of SO_2 on the untreated filter used to trap particulate sulphate. Although the filters have been retained for future analysis, the changed performance of the bubbler from mid 2002 may make this difficult to assess with the samples presently available.

2.3.3. PERFORMANCE AGAINST OTHER SAMPLERS

The attempt to explain the offset was unfortunately confounded by the change in the performance of the bubbler technique from Spring 2002, most noticeably at Cwmystwyth and Lough Navar. The daily bubbler measurements of SO_2 at Bush have in the past shown very good agreement with the co-located automatic UV-F measurements [see *e.g.,* Hasler *et al.*, 2000]. However, even at this site, there appeared to be a step change in the baseline of the bubbler at the Bush site from May 2002 when compared to the daily-averaged UV-F measurements, as shown in Figure 2.5. From investigations carried out, it would appear that the changed performance of the bubbler from Spring 2002 can be ascribed to either increasing porosity of or the effects of leaching of sulphate from the walls of the bubbler containers.

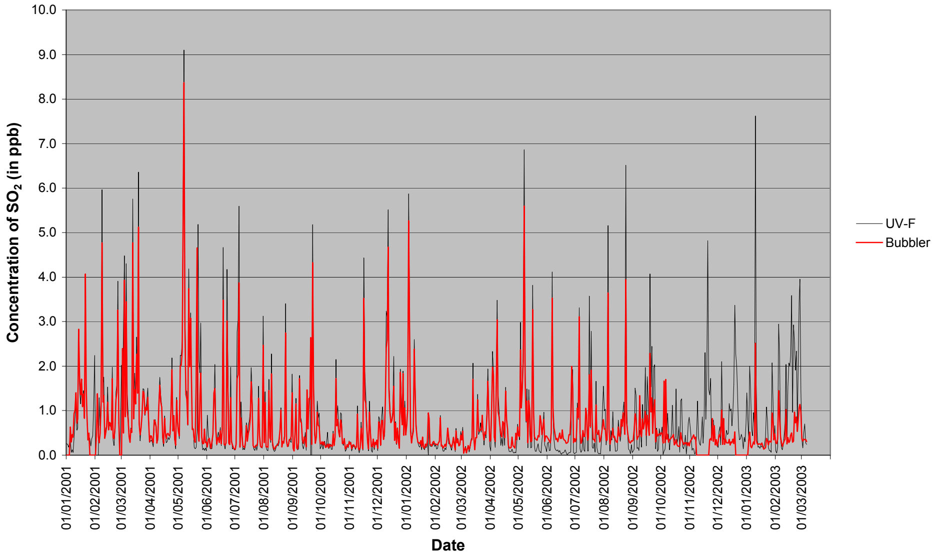

Figure 2.5 - *Comparison of the Bubbler and UV-F SO_2 Measurements Made at Bush.*

There are other measurements which can be used to provide an additional check of the performance of the filter-pack sampler. As part of the Acid Deposition Monitoring programme, measurements of nitric acid and other acid gases are made using a denuder technique on a monthly basis at 12 sites [see *e.g.*, Hayman *et al.*, 2003a]. The monthly SO_2 denuder measurements were compared against the monthly-averaged concentrations derived from the filter-pack and bubbler measurements. Figure 2.6 shows a comparison of the these measurements made at Bush, Lough Navar, Strathvaich Dam and Cwmystwyth.

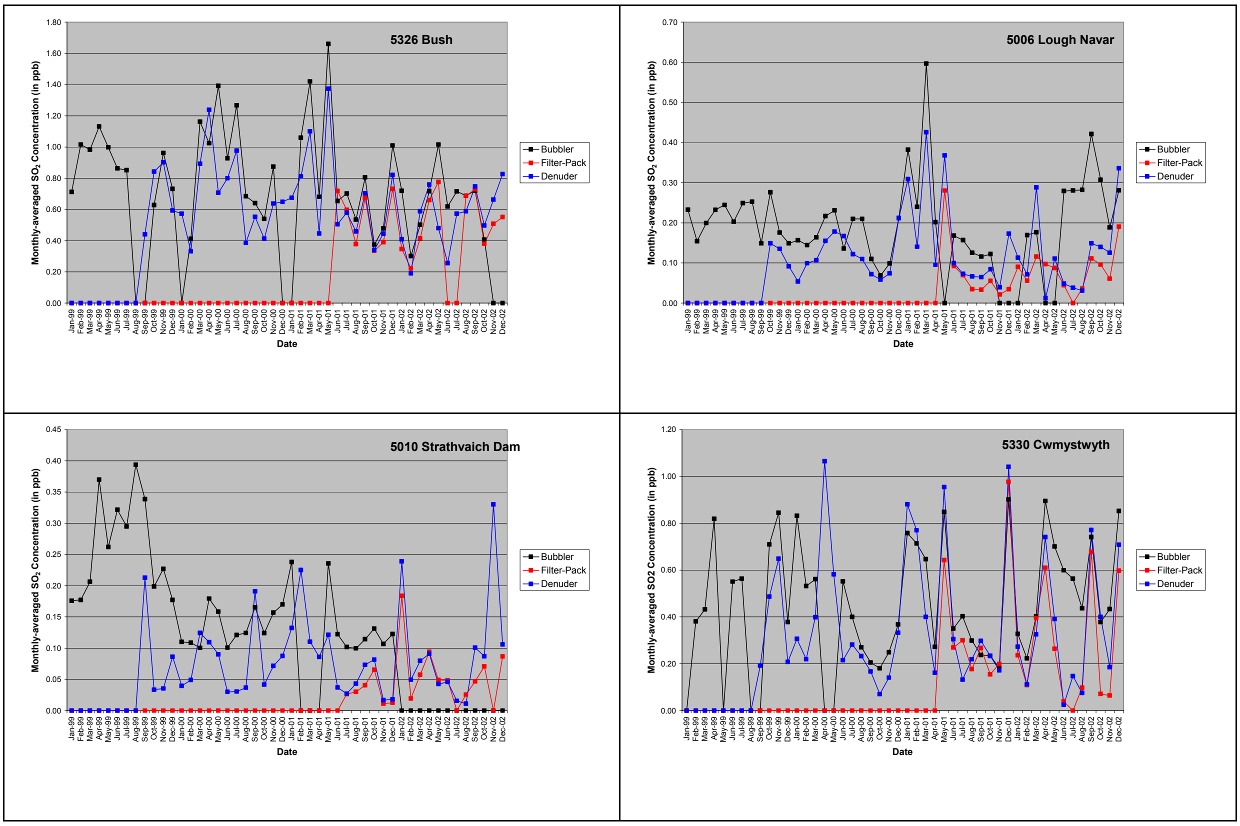

Figure 2.6 - *Comparison of the Monthly-averaged Concentration Measurements made using the Bubbler, Filter-pack and Denuder Techniques.*

This comparison allows the following statements to be made:

- The three samplers generally show the same qualitative behaviour with time
- The filter-pack and denuder measurements are in good agreement although the denuder measurements are slightly larger.
- Both the filter-pack and denuder measurements are lower than those of the bubbler. This is especially noticeable during the period from Spring 2002 when there was a significant discrepancy between the filter-pack and bubbler measurements

2.4. SO_2 Measurements: Results and Discussion

The complete set of measurements made between 1997 and 2001 for the 32 sites in the Rural Sulphur Dioxide Monitoring Network and the 8 sites in the UK Acid Deposition Monitoring Networks can be found in the Annual Data reports prepared on the Rural Sulphur Dioxide Monitoring Network [Hasler *et al.,* 2001; Hayman *et al.*, 2001a, b; Hayman *et al.*, 2003b, c]. The measurements and the reports are also available from Defra's Air Quality Archive site (http://www.airquality.co.uk/archive/index.php).

2.4.1. ANNUAL MEAN CONCENTRATIONS

Annual mean concentrations have been calculated for those sites in the monitoring networks where the data capture was greater than 75% in the calendar year. Table 2.4 provides a summary of the calculated annual mean concentrations. The annual mean concentrations for the years 1997 to 2000 are all based on bubbler measurements. For 2001, the annual mean concentrations are derived from a combination of bubbler and filter-pack measurements. The 2002 data are all derived from filter-pack measurements and these are shown as both the actual and corrected measurements.

Table 2.4 - *Annual Mean Concentrations of Sulphur Dioxide Determined at Network Sites for the Calendar Years 1997 to 2002.*

µg SO_2 m-^{3}

Site		Annual[1,2] mean concentration						
		1997	1998	1999	2000[3]	2001	2002 corrected	2002 uncorrected
Eskdalemuir		1.44	1.08	1.00	0.70	0.89	0.77	0.48
Stoke Ferry		3.80	4.03	2.85	2.28	1.95	1.75	1.46
Lough Navar		0.74	0.61	0.56	0.44	0.55	0.52	0.23
Barcombe Mills		2.77	2.04	1.86	1.71	1.72	1.54	1.25
Yarner Wood		1.76	1.40	1.14	0.85	1.29	0.85	0.57
High Muffles		4.50	3.52	1.85	3.10	3.03	2.77	2.48
Strathvaich Dam		0.85	0.80	0.70	0.36	0.40	0.46	0.17
Glen Dye		1.46	0.96	0.78	0.71	1.01	0.88	0.59
Bush		3.83	2.60	2.33	2.37	2.32	1.77	1.49
Brockhill 1	4	4.89	2.87	2.05	2.69 r	..		
Caenby 1		6.46	7.90	6.42	6.49 r	5.45	4.67	4.39
Camborne 1		2.21	1.82	1.51	1.28 r	1.29	1.05	0.76
Camphill 1		3.14	1.25	1.91	2.23 r	2.10	1.43	1.14
Cardington 2	5	8.75	10.38	8.54	7.47 r	7.82		
Corpach 1		2.45	1.67	1.20	1.14 r	1.07	0.98	0.69
Cressely 1		3.25	2.10	1.75	1.80 r	2.12	1.46	1.17
Etton 1		7.24	7.06	5.82	4.68 r	..	2.90	2.62
Husborne Crawley 1		5.45	4.71	2.81	2.93 r	3.01	2.50	2.21
Little Horkesley 1		5.53	4.56	3.32	2.98 r	2.58	2.06	1.78
Marshfield 1		3.56	3.20	2.84	2.19 r	3.18	1.91	1.62
Ratcliffe 13	6	7.45	6.68	5.26	5.52 r	4.69		
Rockbourne 1		3.01	2.40	1.71	1.44 r	2.01	1.46	1.17
Wakefield 24		8.09	6.61	5.16	5.07 r	5.15	4.28	4.00
Waunfawr 1		2.00	1.92	1.69	1.52 r	3.38	1.65	1.36
Fort Augustus 2		0.67	1.24	..	..	0.28	0.52	0.23
Loch Leven 2		4.89	3.84	3.38	2.52 r	2.52	3.76	3.48
Redesdale 2		2.55	1.73	2.76	2.07 r	0.63	1.95	1.66
Hebden Bridge 2		7.82	4.90	3.77	3.39 r	3.37	2.26	1.97
Preston Montford 2		3.86	2.23	1.86	1.18 r	2.24	1.48	1.19
Bentra		4.15	3.35	..	2.70 r	2.81	1.79	1.50
Pitlochry		1.36	..	0.75	0.47 r	0.59	0.82	0.53
Cam Forest/Formoyle	7	1.52	..	..	0.89 r	0.58	0.61	0.33
Cwmystwyth		2.77	2.07	1.72	1.18 r	1.29	1.01	0.72
Rosemaund		2.55	2.70	2.03	1.34 r	1.28	1.17	0.88
Fairseat		4.23	3.72	4.24	2.78 r	..	2.47	2.18
Bylchau		2.55	1.80	1.08	0.90 r	1.68	1.29	1.00
Crai		2.53	2.48	1.68	1.38 r	1.85	1.36	1.07
Forsinain		0.56	0.73	0.67	0.60 r	0.40	0.56	0.27
Appleacre		3.51	3.31	2.87	1.65 r	1.59	1.48	1.20
Garrary/Benniguinea		1.06	0.79	0.62	0.52 r	0.67	0.69	0.40
Sutton Bonington	8					..	3.24	2.95
Drayton	4					..	1.72	1.43

Notes:

1 Annual means are given only if the data capture was greater than 75%.

2 An improved sampler was introduced during 2001, and results for 2001 are based on measurements from a mixture of old an new instruments. The 2002 results are almost completely based on the new sampler. The 2001 results have not been corrected but both the uncorrected and corrected results are given for the 2002 measurements.

3 Results for 2000 have been slightly revised due to the introduction of a weighting method to take account of different measurement periods.

4 The sampler at the Brockhill site was moved in early 2002 to a new site at Drayton because of access difficulties.

5 The site at Cardington closed in January 2002.

6 The site at Ratcliffe closed in November 2001.

7 The Cam Forest sampler was relocated to Formoyle about 5km away in November 2001 due to building work. Measurements from the two sites have been combined.

8 Sampling at the Sutton Bonnington site commenced in May 2001 using with both the old and new samplers. The 2002 annua mean is based on the measurements made with the new sampler.

The highest annual mean concentrations in the Rural Sulphur Dioxide Monitoring network are found in the Yorkshire and Nottinghamshire areas (Etton, Wakefield and Caenby). The SO_2 concentrations in these areas are influenced by the present of major emission sources.

High concentrations are also observed at the Cardington site which is situated close to a very local source. The lowest annual mean concentrations were measured at sites in Scotland and Northern Ireland: Fort Augustus, Forsinain, Strathvaich Dam and Lough Navar. All of these sites are located in more remote and less populated areas of the UK, away from the direct influence of SO_2 emission sources.

Overall, SO_2 concentrations in rural areas have decreased between 1997 and 2002. Much of the decrease can be associated with the decline in UK SO_2 emission estimates during this period [Dore, 2002]. Figure 2.7 presents both the monthly and running annual mean SO_2 concentrations measured at Eskdalemuir. This is used as an example to illustrate the substantial decline in SO_2 concentrations which have occurred since the early 1980s. The average concentration at Eskdalemuir has decreased by a factor of ten since 1980 from 4.5 ppb to 0.3 ppb. Figure 2.7 shows that the downward trend in the SO_2 concentrations follows the reduction in UK SO_2 emissions.

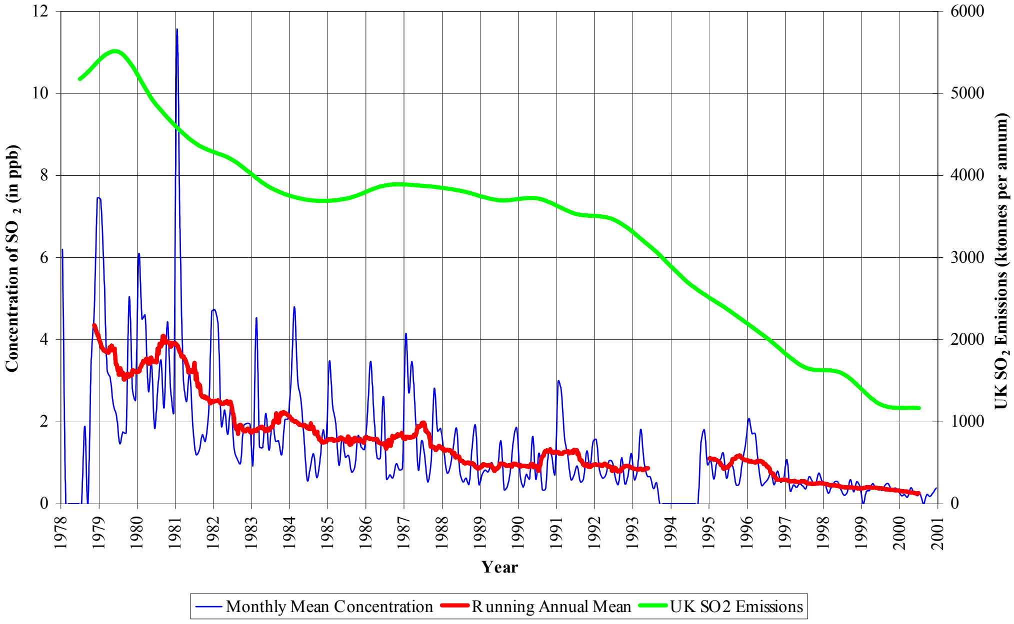

Figure 2.7 - *Trends in the Concentration of Sulphur Dioxide observed at Eskdalemuir since 1978 and in the Annual UK Emissions of Sulphur Dioxide.*

Figure 2.7 also suggests that the large seasonal variation, where higher concentrations are observed during cold winter months, are no longer apparent. Higher concentrations are expected during the winter period because of the relatively higher emissions at this time of the year, combined with poorer vertical dispersion of the emissions.

2.4.2. SPATIAL VARIATIONS

The Rural Concentration Field

The sites used to map the rural SO_2 concentration field are sited away from local sources of pollution so that they are representative of the surrounding region. The sites with valid annual mean concentrations were used to derive the distribution of the annual mean SO_2 concentrations using a geostatistical kriging method [Webster *et al.*, 1991]. Other measurements, including those made at the JEP co-ordinated sites in Nottinghamshire, Yorkshire and the Thames Estuary[1], have been used in the production of the concentration maps. The maps, shown in the upper panels of Figure 2.8. for the years 1997 through to 2001, clearly indicate that the highest concentrations are observed in the regions close to the major emission sources (*i.e.*, Yorkshire and the Thames Estuary).

During 2000, the JEP co-ordinated programme was terminated and all the then open sites in Yorkshire were closed, although some were subsequently reopened later in the year by specific power generators. The data capture for these sites in 2000 was therefore well below the 75% threshold so that valid annual mean concentrations could not be derived. As this region has a major impact on the maps produced, a numerical modelling exercise (see Hayman *et al.,* 2003b) was undertaken to calculate the concentration field for this area. The annual mean SO_2 concentration calculated for the Cliffe site was 2.8 ppb and this was used in the production of the concentration maps for 2000.

The Corrected Rural Concentration Field

The maps produced using the rural concentration field alone are not adequate to characterise fully the dry deposition to vegetation in the urban environment, or in rural locations that are on the fringes of urban areas. Hence, the deposition maps prepared using the rural concentration field alone would be inaccurate. A simple methodology has been developed to estimate the correction needed [Stedman *et al.*, 2001a, 2001b].

The approach used has been to take the difference in the urban SO_2 concentration (taken from automatic monitoring instruments in urban background locations) and the corresponding rural background and to correlate this with a simple dispersion of the emissions from line and area sources (*i.e.*, excluding point sources) within a 35 km x 35 km area, weighted by distance and direction from the receptor. The dispersion coefficients derived are then applied to the line and area sources in the National Atmospheric Emission Inventory to give the urban enhancement for each 1 km x 1km grid square covering the UK. As the approach excludes the emissions from the major point sources, it is appropriate to include the JEP sites in the derivation of the base rural concentration field. However, sites such as Cardington which are unduly influenced by local sources have been excluded.

The lower panels of Figure 2.8 show the corresponding urban-enhanced concentration maps produced for 1997 to 2001. Again, the strong downward trend in annual mean concentration is evident, as shown by the smaller areas of the high concentration regions in the Thames Estuary and in Yorkshire and Nottinghamshire.

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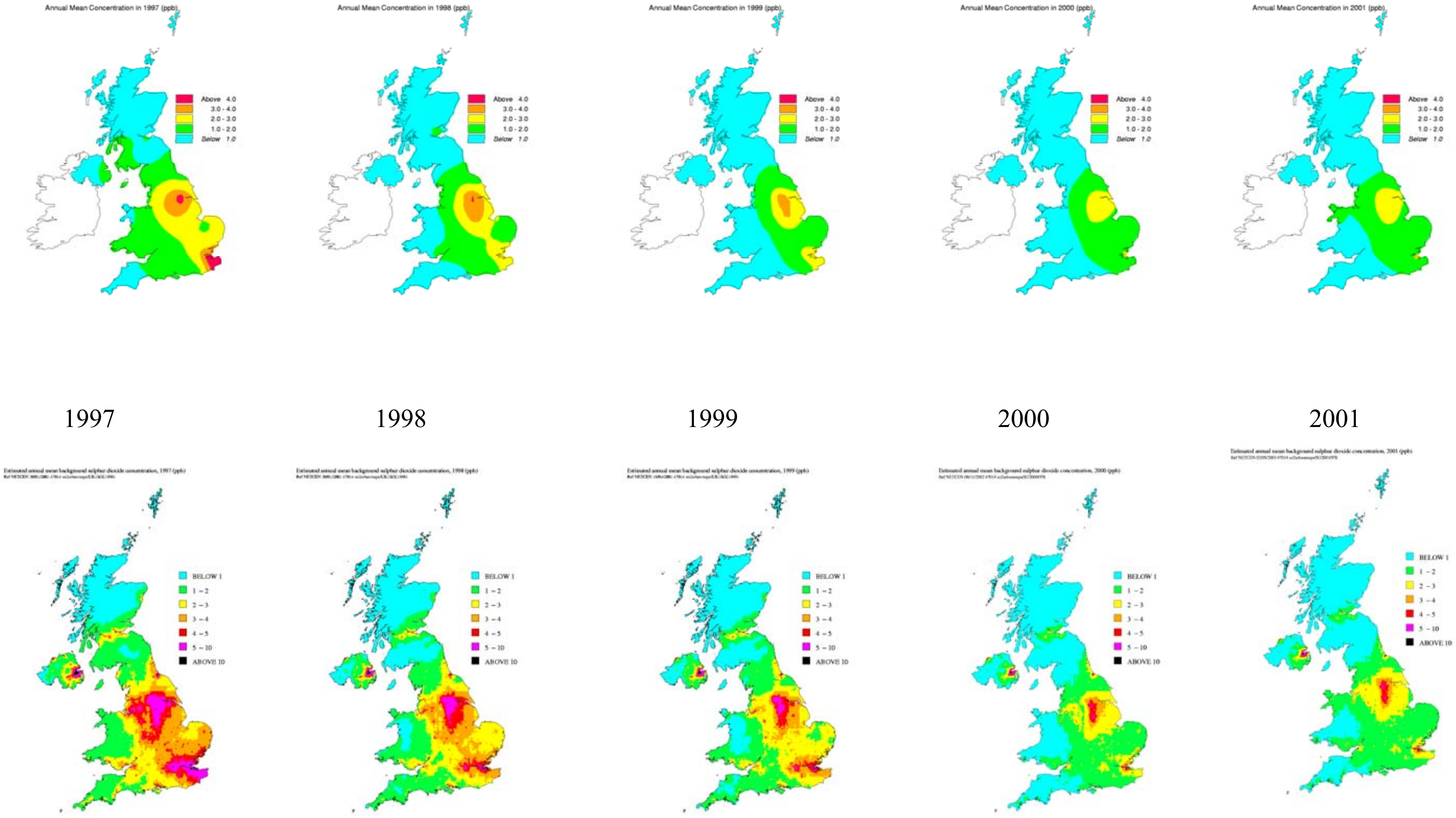
[1] The data for these sites have been provided on condition that neither the measurements made at the sites nor the statistics derived are explicitly reported. The company involved considers that the measurements have commercial value and that a third party could benefit through their inclusion in this report.



1997 1998 1999 2000 2001

Figure 2.8 - Maps of the Underlying (upper panels) and Urban-enhanced (lower panels) Rural SO_2 Concentration Fields (ppb) for 1997 to 2000

2.5. SO_2 concentration mapping (1986-2001)

2.5.1. OBJECTIVE

The objective of the work funded by Defra is to produce a series of annual average SO_2 concentration maps for the UK avoiding bias wherever possible. These concentration maps are used to model the dry deposition of sulphur to different landscapes. Of particular importance with respect to policy is the spatial pattern of sulphur deposition and its interaction with the pattern of ecosystem critical loads, as critical load exceedances are an important element in international emission control negotiations.

The current network of rural SO_2 monitoring sites provides a satisfactory rural concentration field but does not sample the urban areas or their downwind footprint. The reason for providing concentration maps that are not just interpolated rural data is to capture the local effect of these urban sulphur emissions on the surrounding rural concentrations.

2.5.2. BACKGROUND

Rural SO_2 concentrations for the UK over the period 1986 to 2001 were measured at a number of sites. A few sites have automatic monitors or bubblers providing daily data but primarily sites provide weekly, fortnightly or monthly data from bubblers or filter packs. The input for mapping is the annual mean concentration for each site and the number of valid values has generally increased over the period.

Table 2.5 - *No. of valid site annual mean concentrations for each year*

1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001
18	27	25	28	28	25	38	40	6	43	43	44	45	44	42	39

For SO_2, a large proportion of emissions (>80%) are provided by the point sources, including power stations and other large combustion sources burning coal and heavy fuel oil. These sources generate a local field of enhanced SO_2 concentration and the monitoring network, with only around 40 sampling sites, does not capture the fine structure in the concentration field. The urban areas, with their combination of domestic combustion, smaller industrial combustion and vehicles, contribute further to the fine scale variability in the concentration field. In order to better represent the gradients of SO_2 concentration believed to occur in urban/rural landscape mosaics, from 1992 onwards an urban enhancement has been incorporated into the national SO_2 concentration map using empirical procedures (Stedman et al, 1997). These empirical procedures essentially regress the SO_2 concentrations measured at urban monitors against the interpolated concentrations for these locations using only the rural monitors to determine a relationship with either urban land cover or, latterly, with a spatially disaggregated SO_2 emission inventory using basic assumptions on wind speeds and dispersion heights. The final UK SO_2 concentration map is then a combination of the interpolated rural map and the enhancement generated by the parameters from the regression procedure.

Clearly there is a problem for future scenario work if a significant component of the current SO_2 concentration map relies on a regression which can only be performed on measured data. This study reviews an alternative approach suggested by Abbott and Vincent (1999) using emission inventories and dispersion modelling.

2.5.3. THE PROPOSED DISPERSION MODELLING APPROACH

A standard dispersion model, ADMS-2, was used to transport SO_2 from

a) point sources (processes for which an emission release has been reported by the operator) using information on emission rate, stack height, discharge velocity and discharge temperature; and
b) area sources (on a 1 km x 1 km scale) assuming a uniform distribution of the emission within the 1 km x 1 km x 10 m height box and modelled separately in four categories: industrial, road transport, domestic and other.

Because of uncertainty in the data prior to 1992, the simplification of assuming a constant emission release rate for all years was imposed. Seasonal and diurnal profiles were applied to emissions from power stations and domestic sources and a diurnal profile applied to road transport emissions; other emissions were assumed constant throughout the year. The model assumed no chemical conversion within the plume, no dry deposition of SO_2 and no washout in rain. The meteorological data used in the dispersion model were 10 year average statistical summaries, and, for point sources, data from the nearest of the 15 selected meteorological stations were used. The meteorological data well represents the period from the late 1980s to the mid 1990s (see Vincent (18 Aug 2003), Figure 2).

The model was run using 12 linear trajectories with 30° angular separation. Concentration fields were generated separately for the point and area sources and then a regression of the measured rural site concentrations was used to establish values for parameters A and B in the following equation

$$Measured = A + Modelled_{\text{area\_sources}} + B \times Modelled_{\text{point\_sources}} + Residual$$

where the *Modelled* values are the predicted values for the 1 km x 1 km square containing the site. The site residuals were assumed to be partly associated with errors in the model and partly with contributions from remote sources, e.g. European power plants. A residual map, generated by kriging interpolation of the site residuals for each year, was then included to produce the final mapped value of SO_2 annual mean concentration for each 1 km x 1 km square as

$$SO_2\ conc = A + Modelled\ map_{\text{area\_sources}} + B \times Modelled\ map_{\text{point\_sources}} + Residual\ map$$

Concentration maps for each year from 1986 to 2001 are reproduced using the same colour key for each year in Vincent (18 Aug 2003), pages 4-8.

2.5.4. UK BUDGET COMPARISONS

A useful summary of the overall differences between concentration maps can be provided by calculating the total dry deposition of sulphur to the UK from each concentration map. The deposition was calculated using average meteorology, so that there were no confounding meteorological effects in this procedure.

Table 2.6 provides values for UK emissions and for total deposition to the UK of sulphur by (a) combined wet and cloud deposition, and (b) dry deposition. The dry deposition was calculated from 3 separate concentration maps when available: the empirical urban enhancement refers to concentration maps provided using methods similar to those described in Stedman *et al* (1997), the dispersion model refers to methods in the present study, and the rural dry deposition used a concentration map kriged from the site data provided in Vincent (18 Aug 2003), Table 1. The kriging procedure used an exponential variogram fitted to data from all years, with the nugget fixed at zero, a single range for all years (fitted as 121 km) and the sill allowed to vary (fitted parameter values decreasing from 18.6 in 1986 to 0.7 in 2001). Prior to 1996 the standard models were run at a spatial scale of 20 km rather than the current 5 km

Table 2. 6 - *UK sulphur budget 1986-2001 (in kt of S)*

year	emissions (kt S)	5 km scale deposition				20 km scale deposition	
			dry				dry
		wet+cloud	empirical urban enhancement	dispersion model	rural	wet+cloud	empirical urban enhancement
1986	1940	249		314	388	230	262
1987	1938	233		243	258	226	246
1988	1906	240		185	198	251	234
1989	1849	195		159	189	229	227
1990	1861	192		138	164	226	201
1991	1767	191		182	204	223	231
1992	1731	220		168	162	215	185
1993	1558	189		160	143	186	187
1994	1338	204		146	131	198	159
1995	1182	159		135	126	155	123
1996	1013	178	146	130	124	171	125
1997	833	147	156	99	91	132	102
1998	794	163	124	80	76		
1999	605	146	109	67	63		
2000	578	136	51	58	56		
2001	(558)	129	79	60	60		

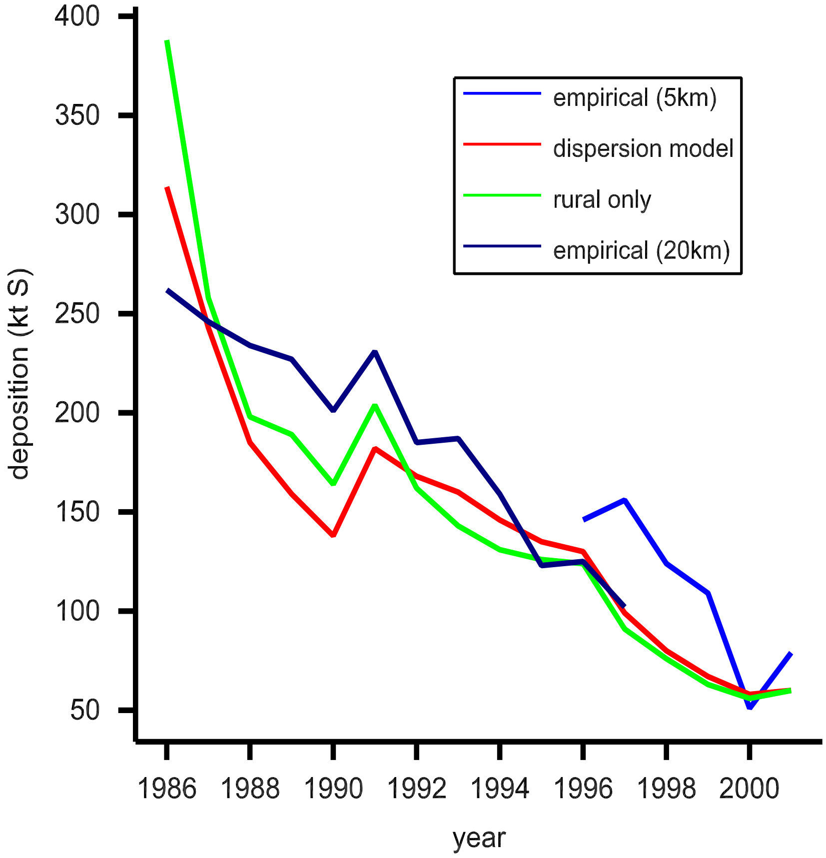


Figure 2.9 - *Total dry deposition to the UK calculated by 4 different methods*

and comparative data are provided from the earlier modelling studies, although there will be differences other than just spatial scale between the two sets of models.

Over the whole period 1986-2001, the dispersion model provides a total dry deposition very similar to that obtained just from the rural interpolated concentration maps. The 'extra' rural sulphur, which was a feature of the empirical methods, has been lost. The interpolation used to provide the rural map for this study relied on a variogram fitted to the entire period, and so it will not replicate maps derived from the rural concentration data for individual years. In any interpretation of Figure 2.9 and of the data in Table 2.6, it should be noted that there were problems with measurements of SO_2 concentration over the period 1993 to 1994 and that the results from the 20 km model after 1992 are likely to be less reliable.

This comparison shows that for the latter period of the study, the dispersion modelling approach has predicted very similar average concentrations to a simpler interpolation of the rural network measurements. However in the earlier period from 1986 to 1991 the dispersion model appears to have reduced the average SO_2 concentration from that which would have been derived from an interpolation of the rural data. The rural measurement network was also smaller during this period and that could be an issue as, when generating interpolated rural maps, the higher predicted SO_2 concentrations may be spread over too large an area.

2.5.5. COMPARISONS OF THE MODELLED OUTPUT WITH SITE DATA

It is possible to compare the measured SO_2 concentration for each site with the mapped value from the dispersion model. The output from the dispersion model is calculated to a 1 km x 1 km scale grid, but the concentrations are input to a deposition model on a 5 km x 5 km scale grid for calculation of budgets and critical loads, etc..

Therefore, the site measurement data were compared to the grid square average of the 5 km x 5 km square in which the site was located in Table 2.7.

Out of 535 comparisons in Table 2.7, the 5 km x 5 km grid square average concentration is greater than the site measured concentration on 334 occasions (62%). The average difference is 0.23 ppb and there is definite evidence of a positive bias shown in the frequency histogram (Figure 2.10). The excess number of positive differences does not appear to have changed during the period (Table 2.8).

Table 2.7 - *Comparison of the site measured SO_2 concentration (in ppb) with the 5 km x 5 km grid square average from the dispersion model*

(SO_2 is the site measured concentration;

map is the 5 km x 5 km grid square average from the dispersion model;

D is the difference (map-SO_2) and the yellow background indicates SO_2> map.)

	1986			1987			1988			1989		
site	SO_2	map	D	SO_2	map	D	SO_2	map	D	SO_2	map	D
Eskdalemuir	1.1	1.2	0.1	1.7	1.7	0.0	1.0	1.0	0.0	1.0	1.0	0.0
Goonhilly	1.6	1.6	0.0	1.6	1.5	-0.1		0.3			0.5	
Stoke Ferry	4.3	4.3	0.0	4.5	4.3	-0.2	3.4	3.2	-0.2	3.4	3.3	-0.1
Lough Navar	0.8	0.7	-0.1	1.1	1.0	-0.1	0.8	0.8	0.0	0.5	0.4	-0.1
Barcombe Mills	4.3	5.6	1.3	3.1	4.1	1.0	2.6	3.7	1.1	2.4	3.4	1.0
Yarner Wood		1.9		2.8	2.7	-0.1	1.4	1.4	0.0	1.4	1.4	0.0
High Muffles		4.3		5.5	5.5	0.0	4.0	4.0	0.0	3.8	3.8	0.0
Strathvaich Dam		2.6		0.7	0.7	0.0	0.5	0.5	0.0	0.3	0.3	0.0
Glen Dye		2.6		1.2	1.2	0.0	0.8	0.8	0.0	0.9	0.9	0.0
Brockhill		6.9		7.9	8.6	0.7	3.6	4.5	0.9	1.4	2.4	1.0
Burham	11.5	12.8	1.3	6.9	7.9	1.0	7.0	8.0	1.0	6.1	6.9	0.8
Caenby	7.7	8.7	1.0	6.4	7.2	0.8	4.8	5.5	0.7	4.5	5.0	0.5
Camborne	3.2	3.5	0.3	1.5	1.8	0.3	1.0	1.2	0.2	1.2	1.4	0.2
Camphill		3.9			2.7		1.8	2.4	0.6	1.8	2.3	0.5
Bentra		8.0			6.7		4.2	6.2	2.0	3.2	6.2	3.0
Corpach		4.4		0.5	1.7	1.2	0.4	1.6	1.2	0.5	1.6	1.1
Cresselly	2.7	2.6	-0.1	2.2	2.2	0.0	1.4	1.4	0.0	1.6	1.6	0.0
Etton		6.2		3.9	3.4	-0.5	3.1	2.7	-0.4	3.7	3.1	-0.6
Harwell		5.3		4.4	4.8	0.4	3.0	3.4	0.4	3.8	4.1	0.3
Husborne Crawley	8.1	8.4	0.3	6.8	7.0	0.2	5.5	5.8	0.3	4.9	5.2	0.3
Inverkip	3.7	3.7	0.0	2.2	2.2	0.0		1.7			1.7	
Kilpaison Burrows	3.4	4.7	1.3		5.2			4.6			3.4	
Little Horkesley	9.8	9.9	0.1	4.2	4.3	0.1	3.7	3.8	0.1	3.4	3.6	0.2
Marshfield	4.6	7.1	2.5	4.5	6.7	2.2	3.3	4.4	1.1	3.2	4.6	1.4

Ratcliffe	12.2	10.2	-2.0	11.2	9.0	-2.2	10.7	9.2	-1.5	8.9	6.7	-2.2
Rockborne		3.7		2.0	2.1	0.1	1.5	1.6	0.1	1.6	1.7	0.1
Wakefield	11.5	14.2	2.7	8.1	10.9	2.8	7.8	10.5	2.7	6.4	9.3	2.9
Waunfawr		2.9		2.4	2.7	0.3	1.2	1.5	0.3	1.1	1.3	0.2
FortAugustus		2.8			0.6			0.4			0.4	
Loch Leven		6.4			5.3			4.5			4.5	
Redesdale		2.1			2.6			1.7			1.5	
Hebden Bridge		7.0			5.0			4.3			3.3	
Preston Montford		3.8			4.1			2.1			0.6	
Pitlochry		3.2			1.5			1.1			1.2	
Bush		6.4			5.4			4.9			4.6	
Great Dun Fell		2.5			2.7			1.8			1.4	
Wharleycroft		3.2			3.2			2.3			1.8	
Cam Forest		2.3			1.8			1.4			1.2	
Cwmystwyth		2.0			2.2			0.8			0.3	
Rosemaund		3.6			4.7			2.0			0.8	
Forsinard		2.6			0.8			0.6			0.5	
Fairseat		9.6			5.6			5.3			4.6	
Bylchau		2.7			2.5			1.2			0.5	
Crai		2.4			2.6			1.3			1.0	
Appleacre		3.2			3.2			2.3			1.8	
Forsinain		2.6			0.8			0.6			0.5	
Benniguinea		1.7			1.6			1.0			0.9	
Bottesford	9.9	9.3	-0.6	11.2	7.7	-3.5		6.4		12.0	5.4	-6.6
Jenny Hurn	9.8	10.2	0.4	11.8	8.5	-3.3		6.9		11.6	6.6	-5.0
Lullington Heath		3.8			2.3			1.7			1.7	
Ladybower		7.3			5.2			4.8		8.0	3.5	-4.5
Rochester		11.5			6.7			6.4			5.1	
Narbeth		2.6			2.2			1.3			1.6	
Wicken Fen		6.5			4.7			3.8			3.4	

	1990			1991			1992			1993		
site	SO_2	map	D	SO_2	map	D	SO_2	map	D	SO_2	map	D
Eskdalemuir	0.8	0.8	0.0	1.3	1.3	0.0	0.9	0.9	0.0	0.8	0.8	0.0
Goonhilly		0.1			0.0			0.2			0.2	
Stoke Ferry	3.5	3.3	-0.2	3.2	3.0	-0.2	2.9	2.7	-0.2	2.4	2.2	-0.2
Lough Navar	0.7	0.7	0.0	0.5	0.5	0.0	0.5	0.5	0.0	0.4	0.4	0.0
Barcombe Mills	1.8	2.8	1.0		0.8			1.4		2.9	4.0	1.1
Yarner Wood	1.3	1.3	0.0	1.7	1.7	0.0	1.1	1.0	-0.1	1.1	1.1	0.0

High Muffles	3.6	3.6	0.0	4.2	4.3	0.1	4.0	4.0	0.0	4.5	4.6	0.1
Strathvaich Dam	0.4	0.4	0.0	0.5	0.5	0.0	0.3	0.3	0.0	0.3	0.3	0.0
Glen Dye	1.6	1.5	-0.1	1.0	1.0	0.0	0.9	0.8	-0.1	0.7	0.7	0.0
Brockhill	0.9	1.9	1.0		4.2		3.2	4.0	0.8	3.7	4.4	0.7
Burham	3.6	4.5	0.9	3.1	3.7	0.6	2.3	3.5	1.2	2.1	3.4	1.3
Caenby	4.0	4.6	0.6	4.5	6.1	1.6	5.9	6.8	0.9	5.9	6.7	0.8
Camborne	0.7	0.9	0.2	0.6	0.8	0.2	0.8	1.0	0.2	0.8	1.0	0.2
Camphill	1.2	1.7	0.5	1.9	2.5	0.6	1.4	2.0	0.6	1.3	1.9	0.6
Bentra	3.4	5.8	2.4	3.9	6.7	2.8	2.7	6.9	4.2	2.5	6.9	4.4
Corpach	0.4	1.5	1.1	0.9	2.0	1.1	0.9	2.0	1.1	0.5	1.7	1.2
Cresselly	1.2	1.3	0.1	1.1	1.0	-0.1	0.8	0.8	0.0	1.4	1.4	0.0
Etton	2.2	1.7	-0.5	1.5	4.4	2.9	3.5	3.2	-0.3	3.8	3.6	-0.2
Harwell	3.3	3.6	0.3		1.6			1.3			1.6	
Husborne Crawley	3.4	3.7	0.3	3.0	3.3	0.3	2.3	2.5	0.2	2.0	2.2	0.2
Inverkip		1.1			1.7			1.3			1.2	
Kilpaison Burrows		2.9			2.8			2.6			3.1	
Little Horkesley	2.2	2.3	0.1	2.3	2.4	0.1	2.0	2.2	0.2	1.8	1.9	0.1
Marshfield	2.9	4.3	1.4	3.7	5.3	1.6	3.1	4.4	1.3	3.0	4.3	1.3
Ratcliffe	8.5	6.4	-2.1	9.1	7.2	-1.9	8.4	6.9	-1.5	5.7	4.7	-1.0
Rockborne	1.6	1.7	0.1	1.7	1.7	0.0	1.4	1.5	0.1	1.4	1.5	0.1
Wakefield	5.3	7.9	2.6	7.0	10.0	3.0	6.3	9.4	3.1	5.4	8.6	3.2
Waunfawr	0.9	1.1	0.2	1.4	1.7	0.3	1.1	1.4	0.3	0.9	1.2	0.3
FortAugustus		0.5			0.7		0.6	0.6	0.0	0.4	0.4	0.0
Loch Leven		4.8			5.6		2.6	5.1	2.5	2.4	4.8	2.4
Redesdale		1.5			1.8		1.1	1.0	-0.1	1.0	1.0	0.0
Hebden Bridge		2.6			5.6		5.9	6.1	0.2	3.6	4.0	0.4
Preston Montford		0.2			2.4		1.8	1.0	-0.8	1.8	1.0	-0.8
Pitlochry		1.3			1.3		0.6	0.9	0.3	0.6	0.9	0.3
Bush		4.3			4.9		1.8	4.8	3.0	2.0	4.8	2.8
Great Dun Fell		1.2			1.9		1.6	1.6	0.0	1.9	1.9	0.0
Wharleycroft		1.5			2.4		2.7	2.9	0.2	2.5	2.7	0.2
Cam Forest		1.1			1.3		1.0	1.2	0.2	1.1	0.9	-0.2
Cwmystwyth		0.0			0.8		1.7	1.7	0.0	1.9	1.9	0.0
Rosemaund		0.4			2.0		2.5	2.7	0.2	2.4	2.6	0.2
Forsinard		0.8			0.6			0.4		0.3	0.3	0.0
Fairseat		2.6			1.5			1.6			2.1	
Bylchau		0.3			2.0			1.4			1.0	
Crai		0.7			1.4			1.5			1.7	

Appleacre		1.5			2.4			2.9			2.7	
Forsinain		0.8			0.6			0.4			0.3	
Benniguinea		0.5			1.2			0.9			0.7	
Bottesford	11.1	5.1	-6.0	11.2	8.0	-3.2	10.4	8.4	-2.0	8.7	7.4	-1.3
Jenny Hurn	12.4	6.2	-6.2	13.3	12.5	-0.8	10.7	10.4	-0.3		9.9	
Lullington Heath		1.1			0.0			0.0		2.0	2.2	0.2
Ladybower	6.6	3.0	-3.6	9.8	9.8	0.0	8.3	8.4	0.1	7.0	7.9	0.9
Rochester		3.0			2.4			4.2			3.8	
Narbeth		1.2			1.0			0.8			1.4	
Wicken Fen		2.8			2.9			2.5			2.0	

	1994			1995			1996			1997		
site	SO_2	map	D	SO_2	map	D	SO_2	map	D	SO_2	map	D
Eskdalemuir		1.1		0.9	0.9	0.0	0.9	0.9	0.0	0.5	0.5	0.0
Goonhilly		0.9			0.8			1.8			1.2	
Stoke Ferry		1.3		2.3	2.2	-0.1	1.9	1.9	0.0	1.4	1.4	0.0
Lough Navar		0.7		0.7	0.6	-0.1	0.4	0.4	0.0	0.3	0.3	0.0
Barcombe Mills		3.3		1.8	2.6	0.8	1.9	2.6	0.7	1.0	1.6	0.6
Yarner Wood		0.8		1.4	1.3	-0.1	1.0	1.0	0.0	0.7	0.7	0.0
High Muffles		2.9		2.6	2.6	0.0	2.3	2.3	0.0	1.7	1.7	0.0
Strathvaich Dam		1.3		0.7	0.7	0.0	0.6	0.6	0.0	0.3	0.3	0.0
Glen Dye		1.6		0.8	0.8	0.0	0.9	0.8	-0.1	0.6	0.5	-0.1
Brockhill		2.6		2.6	3.3	0.7	2.4	3.1	0.7	1.8	2.3	0.5
Burham		5.6			5.1			5.4			5.4	
Caenby		5.7		3.0	3.4	0.4	2.3	2.7	0.4	2.4	3.3	0.9
Camborne		1.6		1.2	1.2	0.0	1.4	1.5	0.1	0.8	1.0	0.2
Camphill		2.4		1.5	2.2	0.7	1.4	2.0	0.6	1.2	1.8	0.6
Bentra		6.1		2.4	4.5	2.1	2.2	5.3	3.1	1.6	4.6	3.0
Corpach		2.5		0.9	1.6	0.7	0.9	1.6	0.7	0.9	1.4	0.5
Cresselly		1.0		1.5	1.4	-0.1	1.6	1.5	-0.1	1.2	1.3	0.1
Etton		5.7		3.1	3.1	0.0	3.1	3.0	-0.1	2.7	2.7	0.0
Harwell		0.9			1.8		2.7	1.7	-1.0		0.9	
Husborne Crawley		1.9		3.1	3.3	0.2	2.5	2.5	0.0	2.1	2.1	0.0
Inverkip		1.7			1.3			2.4			1.8	
Kilpaison Burrows		3.1			3.5			3.6			3.4	
Little Horkesley		1.8		2.3	2.3	0.0	2.5	2.5	0.0	2.1	2.1	0.0
Marshfield		3.1		2.7	3.5	0.8	2.5	2.5	0.0	1.3	1.5	0.2
Ratcliffe	4.6	4.1	-0.5	4.4	4.3	-0.1	4.2	5.0	0.8	2.8	2.8	0.0
Rockborne		1.0		1.3	1.4	0.1	1.6	1.7	0.1	1.1	1.2	0.1

Wakefield	3.5	6.3	2.8	3.5	5.8	2.3	3.4	5.2	1.8	3.0	4.7	1.7
Waunfawr		1.4		0.9	1.1	0.2	1.0	1.4	0.4	0.8	1.1	0.3
FortAugustus		1.4		0.6	0.6	0.0	0.6	0.6	0.0	0.3	0.3	0.0
Loch Leven		5.0		2.3	4.2	1.9	1.9	3.8	1.9	1.8	5.3	3.5
Redesdale		1.4		1.1	1.1	0.0	1.7	1.6	-0.1	1.0	0.9	-0.1
Hebden Bridge		2.6		2.6	2.8	0.2	2.9	3.0	0.1	2.9	3.1	0.2
Preston Montford		1.5		2.1	1.6	-0.5	2.3	1.9	-0.4	1.5	1.0	-0.5
Pitlochry		1.7		0.7	0.4	-0.3	0.5	1.8	1.3	0.5	1.4	0.9
Bush		4.5		2.1	3.5	1.4	1.8	3.1	1.3	1.4	2.7	1.3
Great Dun Fell		1.0		1.6	1.6	0.0		1.5			1.0	
Wharleycroft		1.4		1.6	1.7	0.1		2.1			1.5	
Cam Forest		1.4		0.7	0.7	0.0	0.7	0.6	-0.1	0.6	0.5	-0.1
Cwmystwyth		0.4		1.7	1.6	-0.1	1.8	1.8	0.0	1.0	1.0	0.0
Rosemaund		0.9		1.7	1.8	0.1	1.7	1.8	0.1	1.0	1.1	0.1
Forsinard		1.5		0.4	0.4	0.0	0.4	0.4	0.0		0.2	
Fairseat		3.1		2.6	2.9	0.3	3.1	3.4	0.3	1.6	2.1	0.5
Bylchau		1.1		1.9	1.9	0.0	1.0	1.0	0.0	1.0	1.0	0.0
Crai		0.7		1.4	1.4	0.0	1.4	1.4	0.0	1.0	0.9	-0.1
Appleacre		1.4			1.7			2.1		1.3	1.5	0.2
Forsinain		1.5			0.4			0.4		0.2	0.2	0.0
Benniguinea		0.9			0.8			0.9			0.6	
Bottesford	5.1	5.8	0.7	4.5	4.1	-0.4	4.3	4.1	-0.2	2.7	3.7	1.0
Jenny Hurn	5.4	6.0	0.6	4.6	4.9	0.3	3.1	3.3	0.2	4.8	4.8	0.0
Lullington Heath	2.0	2.1	0.1	2.3	2.3	0.0	2.4	2.4	0.0	1.7	1.7	0.0
Ladybower	5.2	5.1	-0.1	4.4	4.4	0.0	4.3	4.2	-0.1	3.7	3.5	-0.2
Rochester		3.3			3.3		4.8	4.2	-0.6	3.9	4.6	0.7
Narbeth		1.0			1.4			1.4		1.2	1.2	0.0
Wicken Fen		1.2			2.1			1.8			1.2	

	1998			1999			2000			2001		
site	so2	map	D	so2	map	D	so2	map	D	so2	map	D
Eskdalemuir	0.4	0.4	0.0	0.4	0.4	0.0	0.3	0.3	0.0	0.3	0.3	0.0
Goonhilly		0.4			0.4			0.3			0.3	
Stoke Ferry	1.5	1.5	0.0	1.1	1.0	-0.1	0.9	0.8	-0.1	0.7	0.7	0.0
Lough Navar	0.2	0.2	0.0	0.2	0.2	0.0	0.2	0.2	0.0	0.2	0.2	0.0
Barcombe Mills	0.8	1.3	0.5	0.7	1.1	0.4	0.6	0.9	0.3	0.6	1.0	0.4
Yarner Wood	0.5	0.5	0.0	0.4	0.4	0.0	0.3	0.3	0.0	0.5	0.5	0.0
High Muffles	1.3	1.4	0.1	0.7	0.7	0.0	1.2	1.2	0.0	1.1	1.2	0.1
Strathvaich Dam	0.2	0.2	0.0	0.3	0.3	0.0	0.1	0.1	0.0	0.2	0.2	0.0

Glen Dye	0.3	0.3	0.0	0.3	0.3	0.0	0.3	0.3	0.0	0.4	0.4	0.0
Brockhill	1.1	1.4	0.3	0.8	1.0	0.2	1.0	1.1	0.1		1.3	
Burham		3.4			3.1			2.2			2.7	
Caenby	3.0	3.4	0.4	2.4	2.9	0.5	2.5	2.9	0.4	2.0	2.4	0.4
Camborne	0.7	0.7	0.0	0.6	0.6	0.0	0.5	0.5	0.0	0.5	0.6	0.1
Camphill	0.5	1.0	0.5	0.7	1.2	0.5	0.8	1.3	0.5	0.8	1.2	0.4
Bentra	1.5	2.8	1.3	1.1	2.4	1.3	1.0	2.0	1.0	1.1	2.4	1.3
Corpach	0.6	1.0	0.4	0.5	0.7	0.2	0.4	0.6	0.2	0.4	0.7	0.3
Cresselly	0.8	0.9	0.1	0.7	0.7	0.0	0.7	0.8	0.1	0.8	0.9	0.1
Etton	2.7	2.4	-0.3	2.2	2.1	-0.1	1.8	1.7	-0.1		1.9	
Harwell	1.4	1.0	-0.4	1.0	0.7	-0.3	1.3	1.1	-0.2	1.2	1.0	-0.2
Husborne Crawley	1.7	1.9	0.2	1.1	1.2	0.1	1.1	1.3	0.2	1.1	1.3	0.2
Inverkip		0.3			0.4			0.5			0.5	
Kilpaison Burrows		2.9			2.4			2.2			2.1	
Little Horkesley	1.7	1.7	0.0	1.2	1.2	0.0		1.1			0.7	
Marshfield	1.2	1.8	0.6	1.1	1.7	0.6	0.8	1.6	0.8	1.2	2.1	0.9
Ratcliffe	2.5	2.1	-0.4	2.0	1.6	-0.4	2.1	1.7	-0.4	1.8	1.6	-0.2
Rockborne	0.9	0.9	0.0	0.6	0.7	0.1		0.8			0.8	
Wakefield	2.5	4.3	1.8	1.9	3.6	1.7	1.9	3.3	1.4	1.9	3.4	1.5
Waunfawr	0.7	0.8	0.1	0.6	0.7	0.1	0.6	0.7	0.1	2.3	0.8	-1.5
FortAugustus	0.4	0.5	0.1		0.3			0.3			0.3	
Loch Leven	1.4	3.4	2.0	1.3	3.2	1.9	1.0	2.7	1.7	0.9	2.8	1.9
Redesdale	0.7	0.7	0.0	1.0	1.0	0.0	0.8	0.8	0.0	0.2	0.2	0.0
Hebden Bridge	1.8	2.0	0.2	1.4	1.6	0.2	1.3	1.4	0.1	1.3	1.4	0.1
Preston Montford	0.8	0.4	-0.4	0.7	0.4	-0.3	0.4	0.3	-0.1	0.8	0.6	-0.2
Pitlochry		0.6		0.3	0.4	0.1	0.2	0.3	0.1	0.2	0.3	0.1
Bush	1.0	1.7	0.7	0.9	1.2	0.3	0.9	1.1	0.2	0.9	1.2	0.3
Great Dun Fell		1.0			0.9			0.5			0.4	
Wharleycroft		1.3			1.1			0.6			0.6	
Cam Forest	0.3	0.3	0.0	0.4	0.4	0.0	0.3	0.3	0.0	0.2	0.2	0.0
Cwmystwyth	0.8	0.8	0.0	0.6	0.6	0.0	0.4	0.4	0.0	0.5	0.5	0.0
Rosemaund	1.0	1.1	0.1	0.8	0.9	0.1	0.5	0.6	0.1	0.5	0.6	0.1
Forsinard		0.3			0.2			0.2			0.2	
Fairseat	1.4	1.6	0.2	1.6	1.8	0.2	1.0	1.2	0.2		1.1	
Bylchau	0.7	0.6	-0.1	0.4	0.4	0.0	0.3	0.3	0.0	0.6	0.6	0.0
Crai	0.9	0.9	0.0	0.6	0.6	0.0	0.5	0.5	0.0	0.7	0.7	0.0
Appleacre	1.2	1.3	0.1	1.1	1.1	0.0	0.6	0.6	0.0	0.6	0.6	0.0
Forsinain	0.3	0.3	0.0	0.3	0.2	-0.1		0.2			0.2	

Benniguinea		0.2			0.3		0.2	0.2	0.0	0.3	0.3	0.0
Bottesford	3.9	3.9	0.0	3.9	3.3	-0.6	2.3	3.4	1.1	2.9	2.8	-0.1
Jenny Hurn	4.0	4.1	0.1	4.0	4.0	0.0	4.6	4.4	-0.2	2.8	3.0	0.2
Lullington Heath	1.4	1.3	-0.1	1.2	1.1	-0.1	1.0	1.0	0.0	1.1	1.1	0.0
Ladybower	2.7	2.6	-0.1	1.8	1.8	0.0	1.6	1.7	0.1	1.9	1.8	-0.1
Rochester	3.2	2.7	-0.5	3.0	2.6	-0.4	2.9	2.6	-0.3	3.1	2.6	-0.5
Narbeth	1.7	0.9	-0.8		0.7			0.7			0.8	
Wicken Fen	1.4	1.5	0.1	1.0	1.1	0.1	0.9	1.0	0.1	0.9	0.9	0.0

Figure 2.10- *Frequency histogram of differences (D) from Table 3*

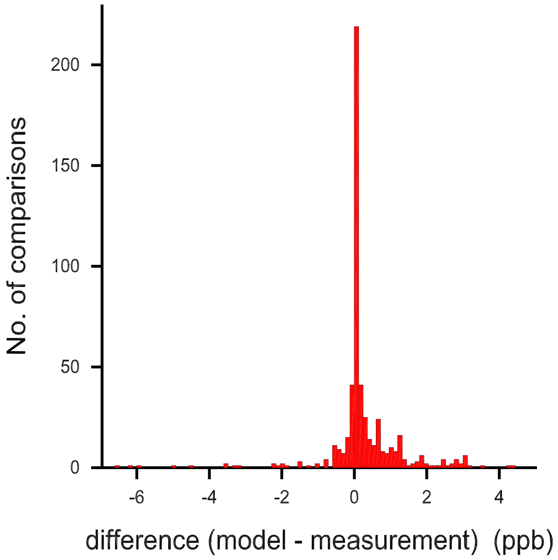


Table 2.8 - *Distribution over years of the difference between mapped and measured values of SO_2 concentration at the monitoring sites*

Year	Positive	Comparisons	% positive differences
1986	13	18	72
1987	16	27	59
1988	18	25	72
1989	19	28	68
1990	17	28	61
1991	15	25	60
1992	25	38	66
1993	25	40	63
1994	4	6	67
1995	24	43	56
1996	23	43	53

1997	29	44	66
1998	28	45	62
1999	25	44	57
2000	29	42	69
2001	24	39	62

Table 2.9a - *Sites with more than 8 years data where the mapped concentration exceeds the measured concentration more than 80% of the time*

Site	Mean difference (ppb)	No. of comparisons	% positive differences
Bentra	2.455	13	100
Wakefield	2.377	16	100
Loch Leven	2.173	9	100
Bush	1.243	9	100
Marshfield	1.108	15	100
Burham	1.007	8	100
Barcombe Mills	0.786	13	100
Corpach	0.785	14	100
Caenby	0.680	15	100
Brockhill	0.645	12	100
Camphill	0.553	13	100
Pitlochry	0.351	8	88
Husborne Crawley	0.206	15	100
Hebden Bridge	0.181	9	100
Camborne	0.143	15	100
Rosemaund	0.111	9	100
Waunfawr	0.107	14	93
Little Horkesley	0.086	13	85
Rockborne	0.076	12	100
High Muffles	0.037	14	93

Table 2.9b - *Sites with more than 8 years data where the mapped concentration is less than the measured concentration more than 80% of the time*

Site	Mean difference (ppb)	No. of comparisons	% positive differences
Etton	-0.015	13	8
Redesdale	-0.034	9	11
Glen Dye	-0.037	14	7
Lough Navar	-0.039	15	7
Stoke Ferry	-0.091	15	13
Preston Montford	-0.440	9	0
Ratcliffe	-0.970	16	6
Bottesford	-1.438	15	20

The sites with consistent differences over the period (Tables 2.9a & 2.9b) show mapped values exceeding measured concentrations across the whole country. There is some possible pattern in the data with the mapped concentration less than the measured concentration at 8 sites, one group close to power generation areas (Preston Montford, Ratcliffe, Bottesford, Stoke Ferry, Etton) and others in remoter locations (Lough Navar, Redesdale, Glen Dye). In several areas, which on initial inspection look to be close to urban areas or downwind of significant pollution, the mapped concentration exceeds the measured concentration and this may be a feature of the proposed modelling approach. Examples include the south of England and south Wales (Campborne, Rockbourne, Barcombe Mills, Burham, Marshfield, Rosemaund, Brockhill, Husborne Crawley, Little Hawksley), some parts of Yorkshire and Lincolnshire (Hebden Bridge, Wakefield, Caenby, High Muffles), central Scotland (Camphill, Bush, Loch Leven) and some sites close to towns or cities (Corpach and Pitlochry (both in Scotland), Bentra (near Belfast, N. Ireland) and Waunfawr (near Bangor, Wales)). Of the 38 sites having more than 8 years data, 8 had consistently lower mapped than modelled concentrations, 20 had consistently higher mapped concentrations, and 10 had no consistent pattern (Ladybower, Yarner Wood, Lullington Heath, Cwmystwyth, Strathvaich Dam, Jenny Hurn, Cam Forest, Harwell, Eskdalemuir, Cresselly).

Monthly mean SO_2 concentrations for 2000 and 2001 are also available from the denuders used in the nitric acid (HNO_3) monitoring network, and for 3 out of the 12 sites this provides an entirely independent check of the mapped concentration (Table 2.10). Where the HNO_3 denuders are on the same site as SO_2 monitoring equipment, the concentrations measured are very similar so this data broadly supports the previous analyses, with the 3 extra sites not adding much extra information.

Table 2.10 - *Comparison of measured and modelled SO_2 concentrations at HNO_3 monitoring network sites (* indicates site not at or near a national SO_2 site)*

	SO2 concentration (ppb)					
	measured		mapped		difference (map-measured)	
HNO_3 network sites	2000	2001	2000	2001	2000	2001
Bush OTC	0.7	0.7	1.1	1.2	0.4	0.5
Glensaugh *	0.3	0.3	0.3	0.4	0.0	0.1
Rothamstead *	1	1.1	1.0	0.9	0.0	-0.2
Strathvaich Dam	0.1	0.1	0.1	0.2	0.0	0.1
Eskdalemuir	0.3	0.4	0.3	0.3	0.0	-0.1
High Muffles	1.3	1.2	1.2	1.2	-0.1	0.0
Stoke Ferry	1.3	0.9	0.8	0.7	-0.5	-0.2
Yarner Wood	0.3	0.5	0.3	0.5	0.0	0.0
Barcombe Mills	0.7	0.7	0.9	1.0	0.2	0.3
Sutton Bonington *	2.1	1.9	2.3	2.1	0.2	0.2
Lough Navar	0.1	0.2	0.2	0.2	0.1	0.0
Cwmystwyth	0.3	0.4	0.4	0.5	0.1	0.1

In summary, there appears to be a small positive bias in that the average difference between the 5 km x 5 km grid square average concentration generated by the model is greater than the concentrations measured at the monitoring sites. There is some indication of a spatial pattern to this bias, although there is no conclusive evidence. The modelled concentrations appear to be too low either in areas with sulphur emitted from high stacks or in areas at some distance from major sources. Closer to low level sources, the modelled concentrations appear to be too high compared to the measurements, and this appears to be the case for a substantial proportion of the network sites.

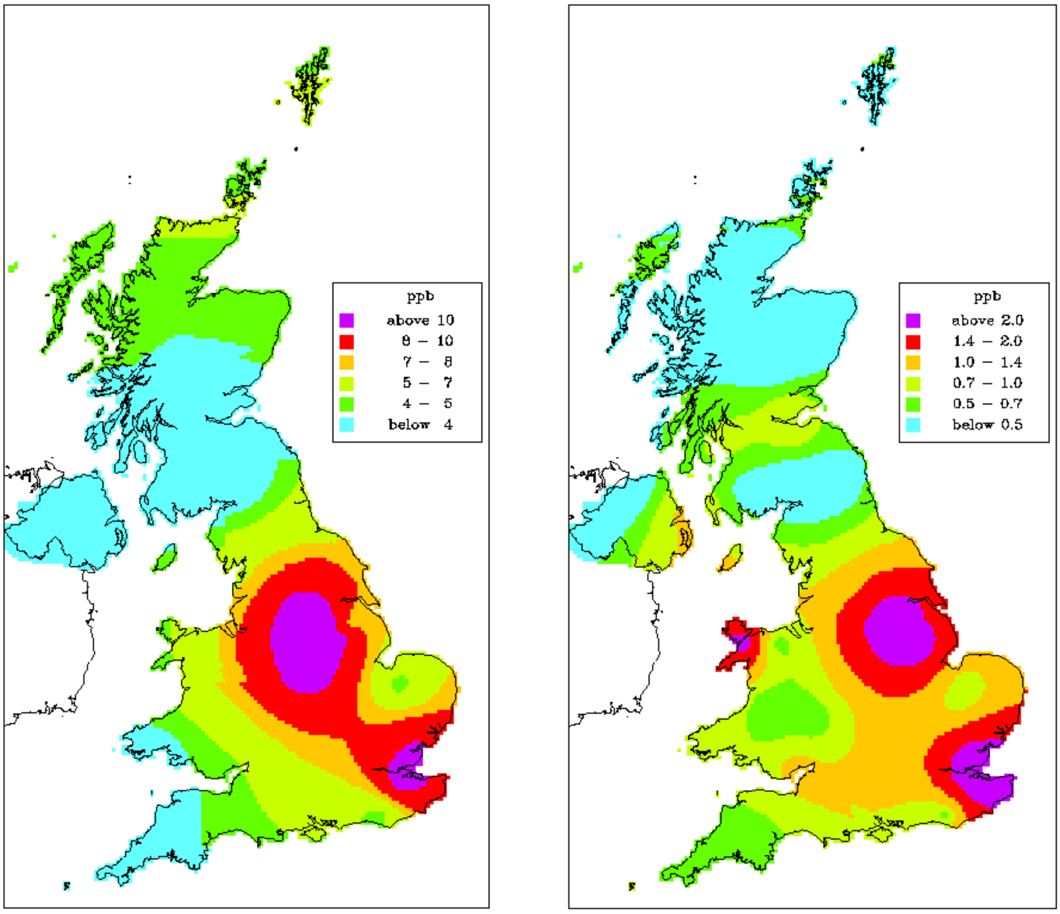
2.5.6. COMPARISON OF THE CONCENTRATION AND DEPOSITION MAPS

The following short description identifies the main features of the latest maps of SO_2 concentration for the UK, using two methods, kriging interpolation of data from the rural measurement stations and dispersion modelling.

The concentration fields produced by interpolation of the measurement data are smoother than by the dispersion modelling procedure. In 1986 (Figure 2.11a), the first year with satisfactory UK coverage, the interpolated map shows a broad elliptical zone, with long axis of 150 km orientated N-S in the English Midlands with annual mean concentrations in excess of 10 ppb SO_2, extending towards a smaller zone, also with concentrations in excess of 10 ppb, in the Thames Estuary. Outside these areas the concentration declines towards the west and north, with coastal areas in the south-west, west and north showing concentrations below 5 ppb. For the year 2001 (Figure 2.11b) the measured concentration field again shows two areas of enhanced concentration, one in the English Midlands (this time centred in the East Midlands with its epicentre close to Sheffield) and one in the Thames Estuary, with annual SO_2 concentrations in excess of 2 ppb, a reduction over the 15 year period by a factor of 5.

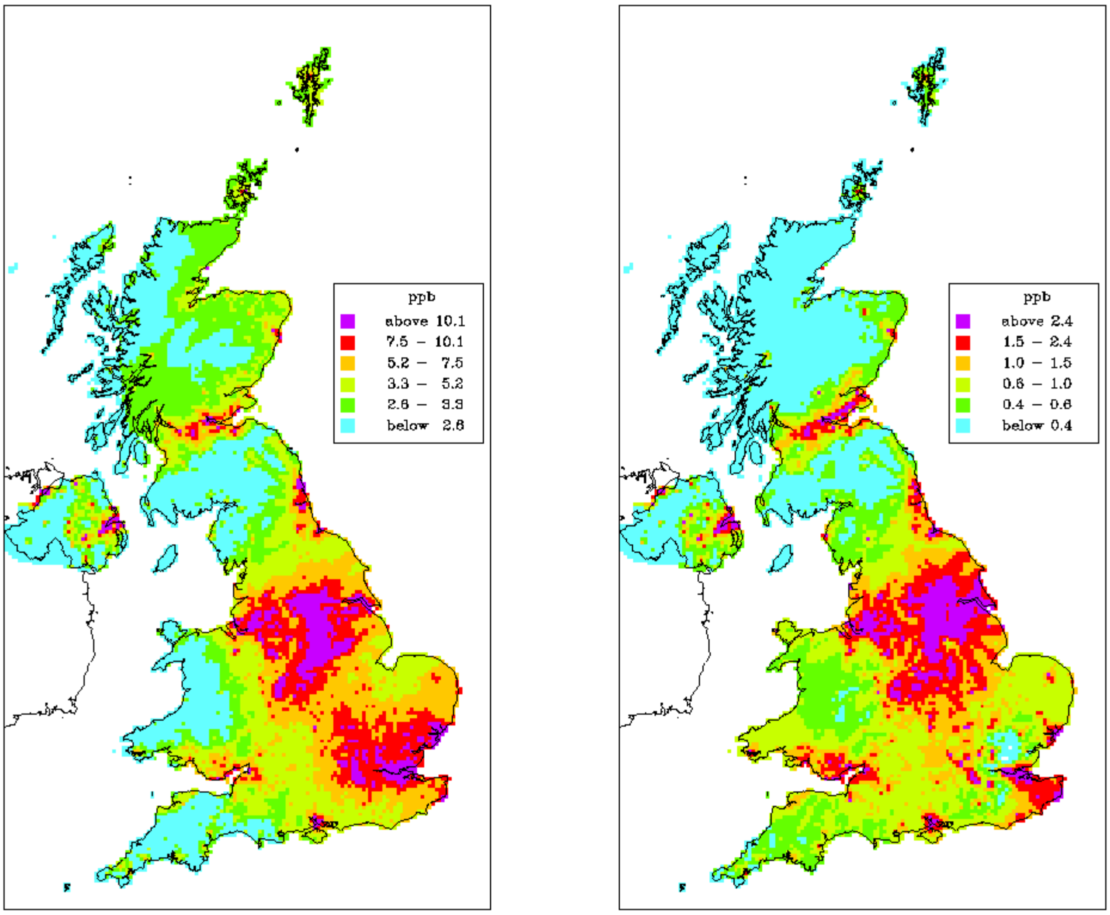
The SO_2 maps produced using dispersion modelling show much more spatial variability, especially close to the sources (Figures 2.11c & 2.11d), but with the concentration level close to sources very similar to those produced by the interpolation of rural concentrations, i.e. a zone in the English Midlands in excess of 10 ppb in 1986 and in excess of 2.4 ppb in 2001. Again the epicentre of the concentration appears a little further east in the later years, and there is a tendency for the model based high concentration areas to show larger values than the measurement based maps in the later years. The other key feature of the maps from dispersion modelling is that many of the other major cities and industrial areas show appreciable

Figure 2.11 - *Maps of the concentration fields from interpolation of the network measurement data and from the dispersion modelling procedure*



(a) 1986 from interpolation

(b) 2001 from interpolation



(c) 1986 from dispersion modelling

(d) 2001 from dispersion modelling

peaks, which are absent from the interpolated rural maps with the relatively low density of measurement sites.

An analysis of the differences between the two approaches may be achieved by differencing the maps from the two methods. The difference maps show increased concentrations in the source regions within 30 km of the major sources and smaller concentrations in the rural areas (Figure 2.12). In the early years (illustrated by 1986 and 1991, Figures 2.12a & 2.12b) the reductions in rural concentrations are large, especially in Wales and the rural areas of western England, but even over northern Scotland the differences are substantial. In the later years, the same features of larger concentrations close to sources and smaller concentrations and deposition than the measurement derived maps in the rural areas are present (illustrated by 1996 and 2001, Figures 4c & 4d), but with smaller absolute differences. The dispersion modelling procedure also creates a radial artefact due to a coarse angular resolution of the wind direction data used in the modelling (30°). This artefact is quite clearly shown in the deposition difference maps for 1996 and 2001 (Figures 2.12c & 2.12d) in the NE of England and in the East Midlands. As the artefact appears to give differences of the order of 0.3 kg S ha^{-1} y^{-1} between adjacent squares depending on whether or not a particular trajectory crosses the square, compared with a median UK sulphur deposition of 2.0 kg S ha^{-1} y^{-1}, the effect is sufficiently large to warrant further investigation and does add extra uncertainty to the deposition estimates.

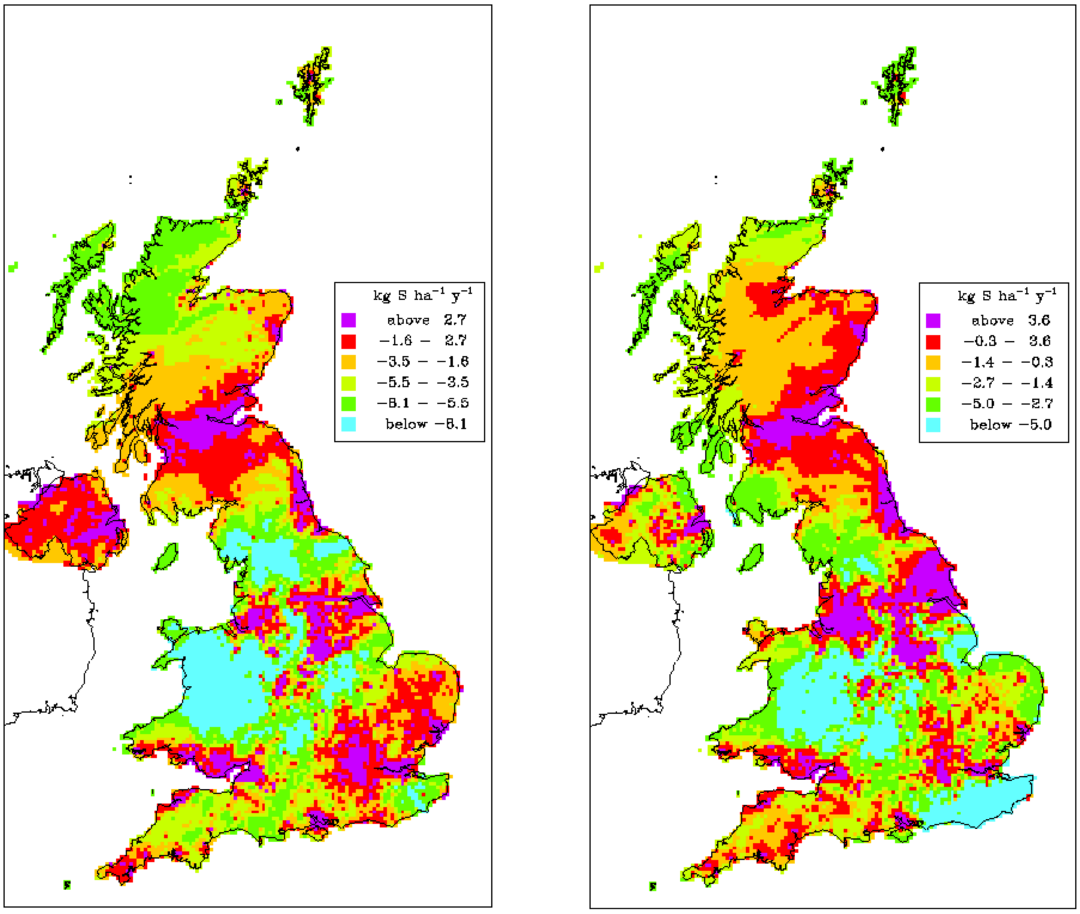
2.5.7. DISCUSSION

The dispersion modelling procedure for producing an SO_2 concentration field for the UK has two major advantages over the interpolated maps from rural measurements. First, it relies on emissions data and so can be used for future scenario work. Secondly, it produces maps which have a structure related to the concept of there being extra sulphur dioxide emissions in populated areas, and these maps are also aesthetically more pleasing in that they reflect current scientific thought that the concentration field of SO_2 is quite variable at a local scale.

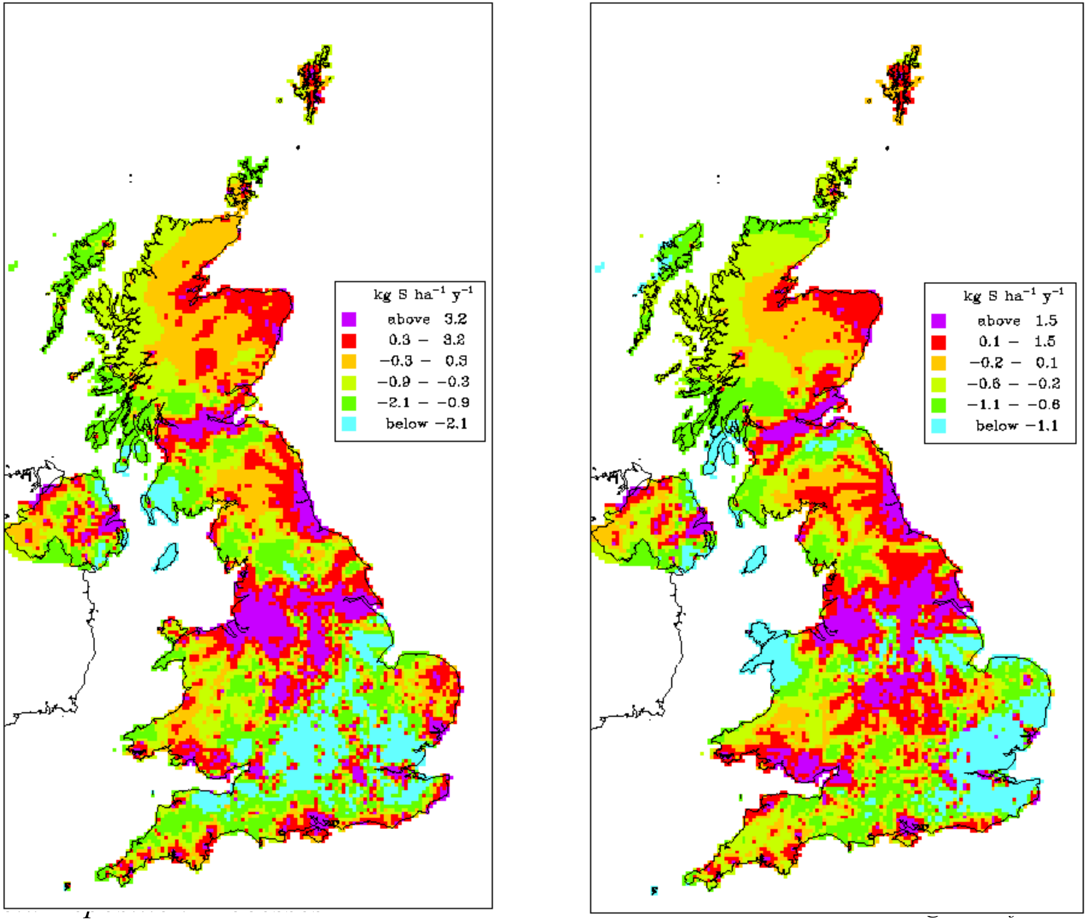
The output from the dispersion modelling procedures should be supported by comparisons with measurement data. Here there is an intrinsic problem. The reason that the urban effects are modelled is that there are few if any sites which capture the supposed gradient in concentration from dense urban area to rural countryside. This is partly a result of an inadequate network size and partly the result of a strategic failure

Figure 2.12 - *Maps of the difference between the dry deposition fields derived from the dispersion modelling procedure and from interpolation of the network measurement data*

(a) 1986 (b) 1991



(c) 1996 (d) 2001



to place sites capturing information on the urban:rural gradient. Therefore, it is difficult to make statements with any degree of certainty about whether or not the dispersion modelling procedure reflects the true gradients in SO_2 concentration near urban areas.

There are several comparisons which can be made between output from the dispersion model and other data. First, the reason for modelling an urban enhancement on the rural concentration field was that there was a belief that the network measurements did not capture the extra SO_2 near to towns. In budget terms, this model actually predicts less deposition of sulphur to the UK than would be estimated by a simple interpolation from rural measurements for the period 1986 to 1991. If the dispersion model budget were correct, then either the relatively sparse rural network from that period was capturing more of the sulphur close to towns than has been assumed so far, or there was no substantial urban enhancement of concentration. Even in the later period of 1996 to 2001 there is only a minimal enhancement over the rural only approach. Philosophically, this current version of a dispersion model does not fit to the scientific theory it was developed to capture - rather than providing additional sulphur it has effectively re-distributed the sulphur with a different spatial pattern.

Secondly, the dispersion model persistently fails over the years to capture the concentrations at a relatively large number of sites, indicating the presence of some degree of bias in the modelling. It appears to underestimate concentrations both close to major industrial sources and at remote sites while overestimating concentrations at network sites relatively close to urban areas. This suggests there is a problem with the atmospheric mixing and with the transport distances in the model. Whether these effects come directly from the model or from the addition of a kriged residual map to compensate for missing emissions is not clear. Certainly for major areas of rural England and the central belt of Scotland, the dispersion model appears to tend to predict higher SO_2 concentrations than were measured at the network sites and at remote sites there are corresponding underpredictions.

Thirdly, the artificial radial effects from the coarse angular resolution of the modelled transects are an issue. This could well be overcome by some local smoothing procedure. However, it also brings up the question as to how much of the relatively attractive representation of local variability in SO_2 concentrations seen on the maps is actually related to this artefact rather than a real representation of a physical process.

2.5.8. CONCLUSION OF REVIEW OF THE PROPOSED DISPERSION MODELLING METHOD

One of the primary purposes of this modelling exercise is to provide an improved SO_2 concentration map for use in public policy decisions, and, in particular, for use in critical load assessments. It is difficult to justify the use of the maps from the dispersion model as presented here as an improvement over the use of an interpolated rural concentration field. There are three basic reasons:

1. it does not provide for any additional sulphur deposition (if there was never really an urban enhancement then the interpolated rural field is quite adequate);
2. it fails to match the measured rural concentrations on too many occasions to conclude that the procedure is unbiassed;
3. the spatial pattern presented cannot readily be supported until artefacts have been removed.

One aspect of this review of concern is that, with the siting criteria from the current networks, adequate information on the urban:rural gradients in SO_2 concentration is not available and it is extremely difficult or impossible to support from measurements any modelling activities which seek to map these effects.

2.5.9. PROVIDING AN ALTERNATIVE APPROACH TO MAPPING SO_2 CONCENTRATIONS IN THE UK

The proposed dispersion modelling exercise has not provided maps of SO_2 concentration which reflect current understanding of the scientific processes involved. There are clearly ways to make improvements to these maps, but meanwhile a set of SO_2 concentration maps for the period 1986 to 2001 is required.

The rural interpolation procedures do predict the site measured concentrations with reasonable accuracy (Figure 2.13), as expected. To recap from the earlier section, the rural interpolated concentration maps were kriged from the measurements using an exponential variogram. There are 3 parameters on an exponential variogram: the nugget was arbitrarily set to 0, the range was fitted to data from all years (121 km), and the sill was allowed to vary between years (decreasing from 18.6 in 1986 to 0.7 in 2001). For any single year there are insufficient data to fit the variogram well.

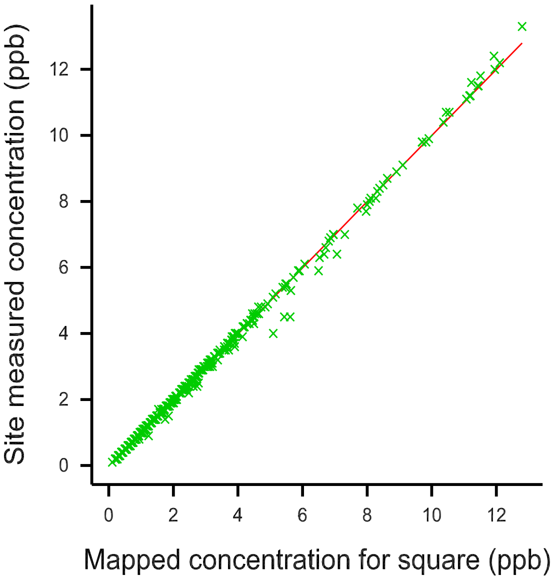


Figure 2.13 - *Comparison of the rural site measurements (1986, ... , 2001) with the interpolated values for the 5 km x 5 km squares containing the sites*

Data are available from the automatic monitoring networks at sites which are classed as urban inner, urban outer, rural, industrial and other. The relationship between these concentrations and the mapped rural concentrations for the 5 km grid square were explored. Extra covariates available were the spatially disaggregated SO_2 emissions for 1999, the point source SO_2 emissions for 1999 and the percentage of urban area in the 5 km square (from the CEH land use classification). These were explored in a variety of combinations including values for the 5 km square, averages over the 5 squares (George cross arrangement), averages over 9 squares (i.e. including diagonals), centre weighted average values, distance and direction to nearest point sources, etc.. Of the available covariates, the percentage of urban area in the square was the most useful.

The problem with deriving an urban enhancement is that, for the map, the objective is to estimate the average SO_2 concentration in the square but the measurements (both rural and urban) do not reflect this average concentration because of the network siting criteria. Even in rural squares with substantial urban area, the siting criteria will attempt to capture the background rural concentration and it appears generally to succeed (see Figure 2.13). An urban excess concentration was calculated for each square with an automatic network measurement site classed as either urban inner or urban outer.

sq_average_conc = prop_rural*rural_conc + prop_urban*urban_conc

urban_additional_conc = sq_average_conc - rural_conc

where the rural_conc was taken from the interpolated rural map and the urban_conc was the annual mean concentration from the automatic site. The square average concentration assumed that the urban concentration was valid for all urban areas in the square and the rural concentration was valid everywhere else. An exponential curve through the origin was fitted for each year to relate urban_additional_conc with the percentage of urban area in the 5 km square (Figure 2.14).

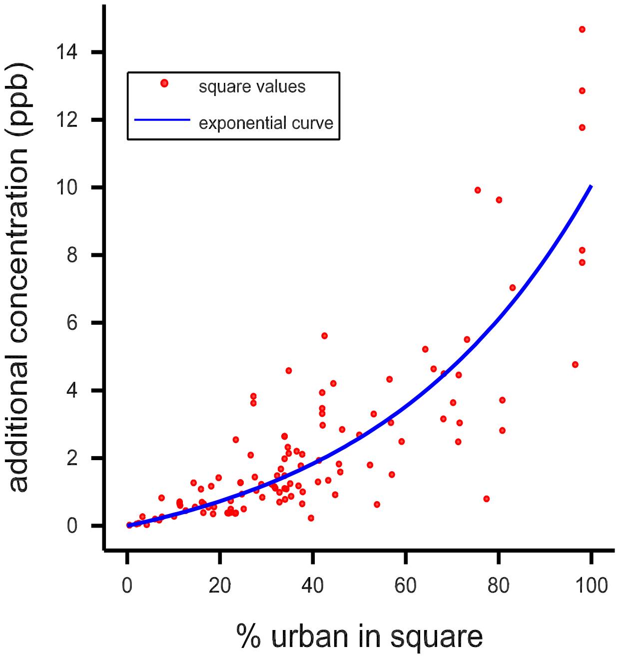


Figure 2.14 - *Exponential relationship for 1999 between the urban additional SO_2 concentration and the percentage of urban area in the 5 km square*

Maps of SO_2 concentration with this extra component added to the rural interpolated maps were produced for 1986 to 2001. The UK budget comparisons for the three methods considered in this study (Table 2.11) show that this additional urban contribution averages 25 kt of S per year over the UK. As with the interpolated rural concentration, the budget dry deposition in 1986 is rather high. In 1986 there were only 18 rural measurement sites, and at 2 of these sites (Burham (TQ730619) and Wakefield (SE352132)) the SO_2 concentration in 1986 was over 3 ppb higher than in any subsequent year. As there was no effective reduction in UK emissions between 1986 and 1987 and as the SO_2 concentrations at the remoter sites showed no change between the 2 years, it is probable that the mapped concentrations by all methods are too high, and that the 1986 UK budget dry deposition should be around 275 kt S. Unless there is further evidence to support the 1986 maps, it is suggested that 1986 be omitted from any trend estimation over the period.

Table 2.11 *Dry deposition to the UK, budget values for 1986-2001 (in kt of S)*

year	interpolated rural	dispersion model	rural with urban addition
1986	388	314	413
1987	258	243	291
1988	198	185	233
1989	189	159	223
1990	164	138	199
1991	204	182	232
1992	162	168	188
1993	143	160	167
1994	131	146	156
1995	126	135	146
1996	124	130	145
1997	91	99	110
1998	76	80	93
1999	63	67	82
2000	56	58	73
2001	60	60	76

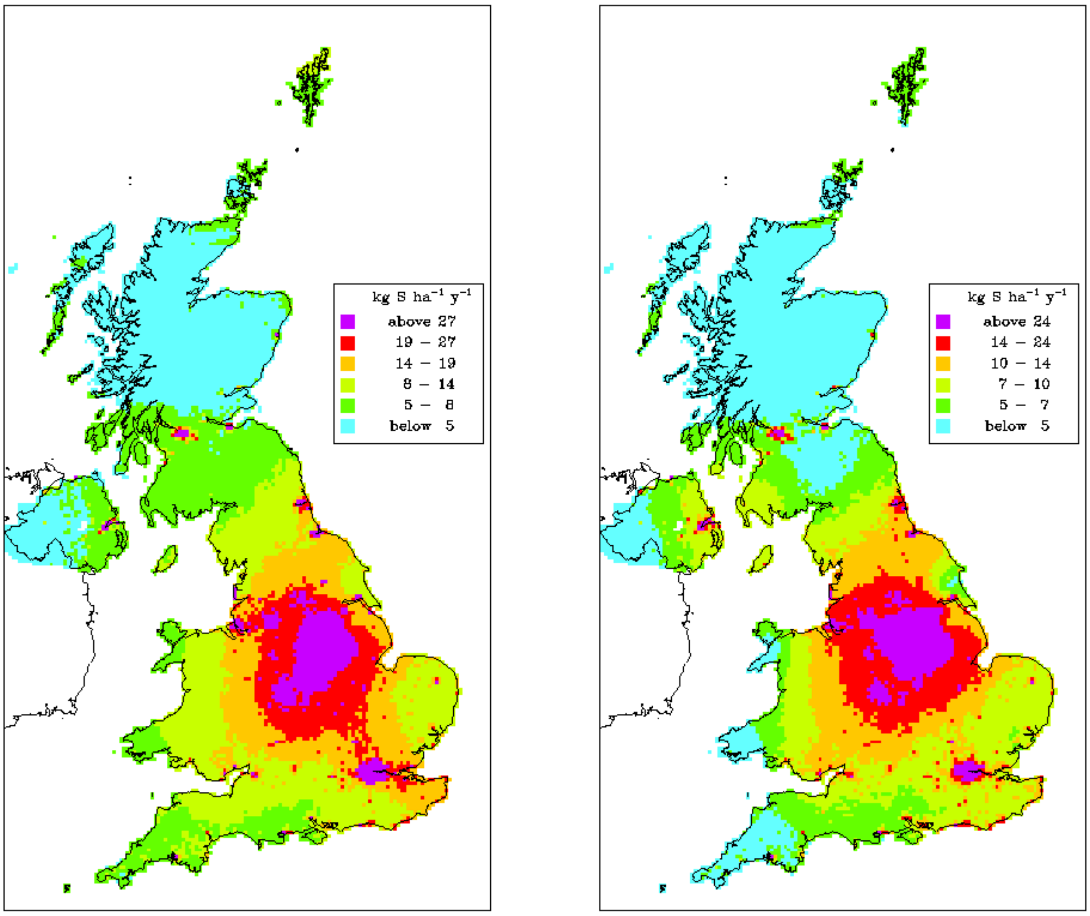
Maps of deposition derived from the urban addition SO_2 concentrations (Figure 2.15) show a decline over the period and the appearance of more 'hot spots' of deposition close to urban sources as the general levels of pollution have decreased. This mapping method is however still sensitive to abnormal patterns from the measurement network, as shown for 2001 by the higher than expected dry deposition in north west Wales. In this respect, however, the method is no different from the methods for producing the maps of wet concentrations used in estimating wet deposition. The unexpected variability in spatial pattern is partly a function of interpolating from a measurement network with rather few sites.

In the interim before further work is available, it seems that this method of producing an urban addition to an interpolated rural concentration field gives a better estimate of deposition to other procedures. In the longer run, it is likely that improvements in the dispersion modelling approach would provide an improved deposition estimate.

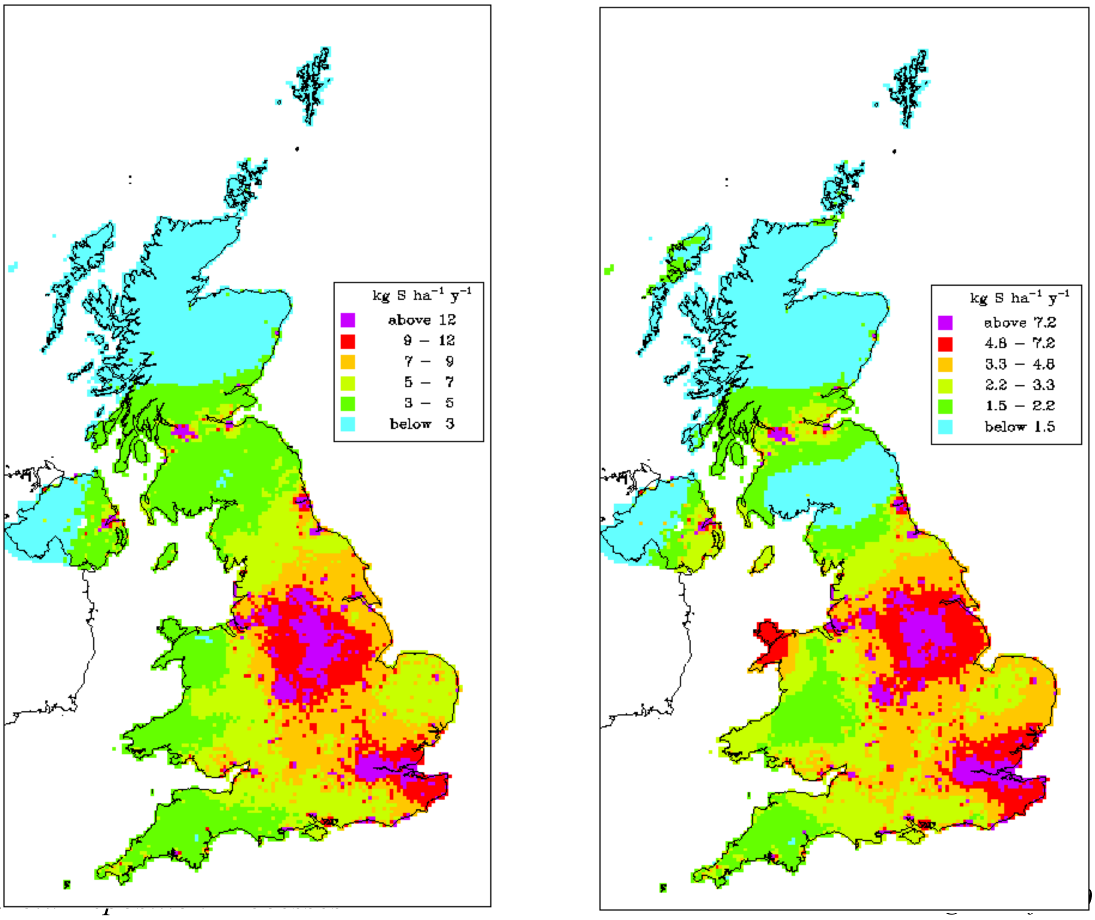
However as background SO_2 concentrations fall, the local modelling of deposition near to sources may be a preferable way forward.

Figure 2.15 - *Maps of sulphur dry deposition using the urban addition to the interpolation rural concentration field*

(a) 1987 (b) 1991



(c) 1996 (d) 2001



2.5. Summary

The following presents the main highlights of this work:

- The monitoring network has continued to provide a high quality dataset for trend analysis and as input to the calculation of deposition budgets although measurements made at remote sites have been close to or below the limits of detection of the bubbler method;
- There is clear evidence of a decline in sulphur dioxide concentrations across the UK
- A new sampler with improved sensitivity has successfully been introduced into the network. The transfer function between the filter-pack and bubbler samplers has been determined as

$$[SO_2]\text{ filter-pack} = 1.049\ [SO_2]\text{ bubbler} - 0.108$$

- Breakthrough has been eliminated as the cause of the offset. The changed performance of the bubbler from Spring 2002 can certainly be ascribed to either increasing porosity of or the effects of leaching of sulphate from the walls of the bubbler containers. It may be that these factors may also explain the underread of the filter-pack sampler against the bubbler method during the early phase of the comparison.

Acknowledgements

With special thanks to all the site operators whose commitment to the network has helped provide such a comprehensive and high quality data set.

Thanks are due to PowerGen and Innogy for supplying data from the JEP Programme.

We would also like to take this opportunity to thank Sandra Hasler and Steve Baker (AEA Technology) for their contributions to the smooth operation of the monitoring networks. We wish them well in their new careers.

Acid Deposition Processes: SO_2 dry deposition

EPG 1/3/166

David Fowler, Mhairi Coyle, Robert Storeton-West, Ron Smith, Jennifer Muller

Centre for Ecology and Hydrology
(Edinburgh Research Station)
Bush Estate, Penicuik,
Midlothian, EH26 0QB, UK.

SO_2 Dry Deposition process studies

- Fluxes of SO_2 have been continuously monitored at two UK sites since 1994 at Auchencorth Moss in Scotland over moorland, and over arable cropland in the English Midlands since 1995.
- At both sites, concentrations of SO_2 have declined, from 1.1 ug SO_2 m^{-3} at Auchencorth Moss in 1995 to 0.8 ugSO_2 m^{-3} in 2001 while at Sutton Bonnington the reduction is larger, from 4 ug m^{-3} to 2 ug m^{-3}.
- The SO_2 deposition fluxes at both sites declined less than concentration because deposition velocities at both sites increased, from 5 to 8 mm s^{-1} at SB and from 4.5 to 6.5 mm s^{-1}at AM.
- The cause of the increase in deposition velocity is a reduction in surface resistance, due to a reduction in the molar ratio SO_2 / NH_3.
- The regional increases in deposition velocity are accelerating the decline in ambient SO_2 concentration and are an important contributor to the changes in S deposition throughout Europe.
- These effects are recognised within EMEP and are parameterised within the EMEP model, improving the model-measurement agreement.

3. DRY DEPOSITION OF SO_2

The objective of this component of the research programme was to monitor rates of SO_2 dry deposition in two areas of the UK and over terrestrial surfaces, which are representative of extensive areas of the country. This has proved necessary because the affinity of terrestrial surfaces for SO_2 have been shown to vary with time due to changes in the chemical composition of the moist film covering vegetation most of the time. The earlier measurements show that as concentrations of SO_2 have declined, the ratio of SO_2/NH_3 has steadily increased, and has resulted in a decrease in the canopy resistance with time (Fowler et al. 2001).

The period of this report covers measurements at two sites, Sutton Bonnington, on arable farmland belonging to the University of Nottingham, 10km SW of the southern boundary of Nottingham and Auchencorth Moss, an extensive area of moorland in the Scottish Borders, 10km SW of the CEH Edinburgh laboratory. The two sites provide measurements of SO_2 concentration, flux, canopy resistance and associated micrometeorological variables used in the measurement and analysis of aerodynamic flux-gradient data.

3.1 Sutton Bonnington

The data series began in 1995 and earlier measurements at this site show that in the 1970s when SO_2 concentrations were in excess of 25ppbV, and about an order of magnitude larger than current values, the canopy resistance was sm^{-1}.

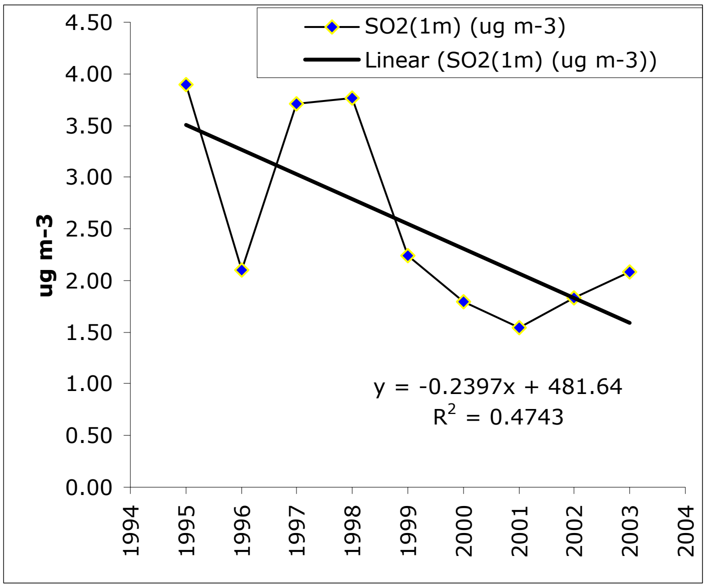


Figure 3.1 Concentrations of SO_2 at a height of 1m above arable cropland at Sutton Bonnington 1995-2003.

The current series of measurements began in 1995, when concentrations averaged 1.5 ppbV (4ug m^{-3}), and have declined steadily through the monitoring period to current values averaging 2 ug m^{-3} (Fig 3.1).

The micrometeorological measurements show small deposition fluxes, in the range 10 to 30 ng SO_2 m^{-3} as shown in Figure 3.2.

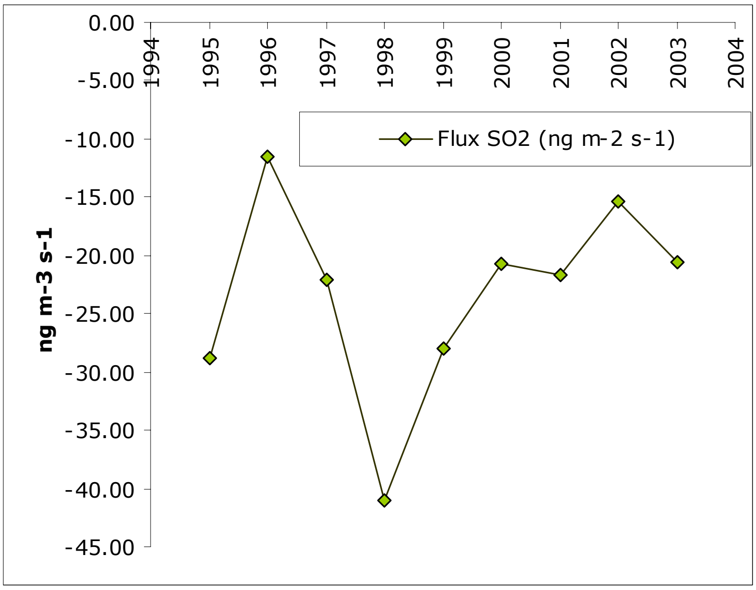


Figure 3 .2 Dry deposition fluxes of SO_2 over arable land in the English Midlands (Sutton Bonnington) 1995 to 2003.

The fluxes are regulated by a combination of transfer processcs, through the lower atmosphere to the vegetation and then onto the vegetation. Each of the steps in the deposition

pathway is characterized by a resistance (Monteith and Unsworth 1980). The average atmospheric resistances, r_a and r_b have not changed with time, even though there are substantial changes between seasons and a considerable inter year variability. However, changes in the surface or canopy resistance (r_c). The change in r_c with time has been noisy as the low concentrations make the flux measurements progressively more difficult. However the canopy resistance has declined from 100 s m^{-1} in 2003 for wheat as shown in Figure 3.2 (values for wheat are not available every year as the field crops are rotated).

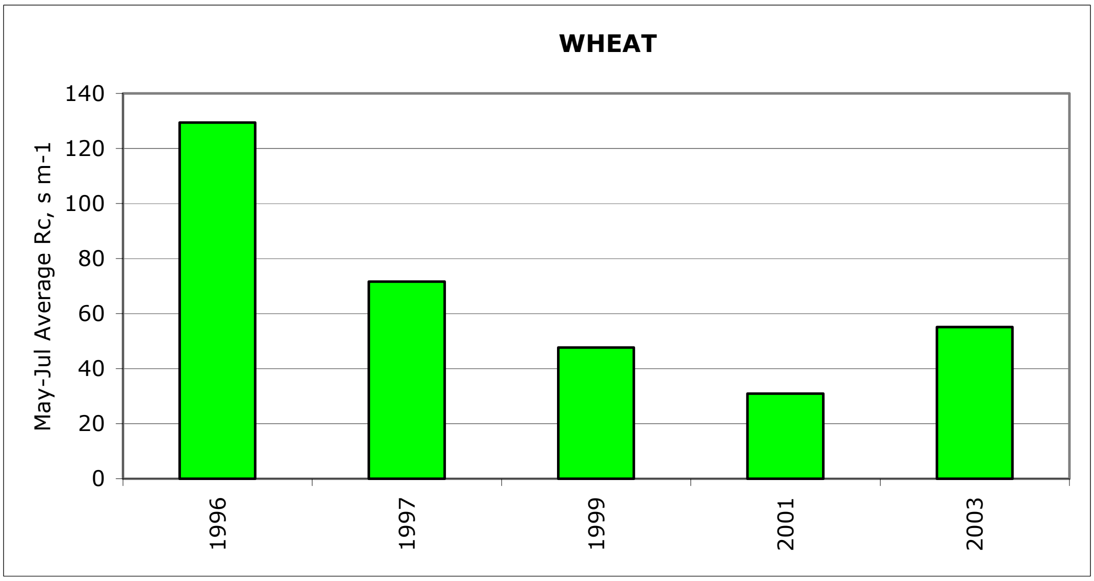


Figure 3.3 Changes in the May-July canopy resistance for SO_2 deposition on Wheat at Sutton Bonnington between 1996 and 2003.

The reduction in canopy resistance with time in the absence of changes in atmospheric resistances leads to an increase in deposition velocity with time, as shown in Figure 3.3 for wheat and 2.4 for the field over the year, including both the crop and bare soil phases.

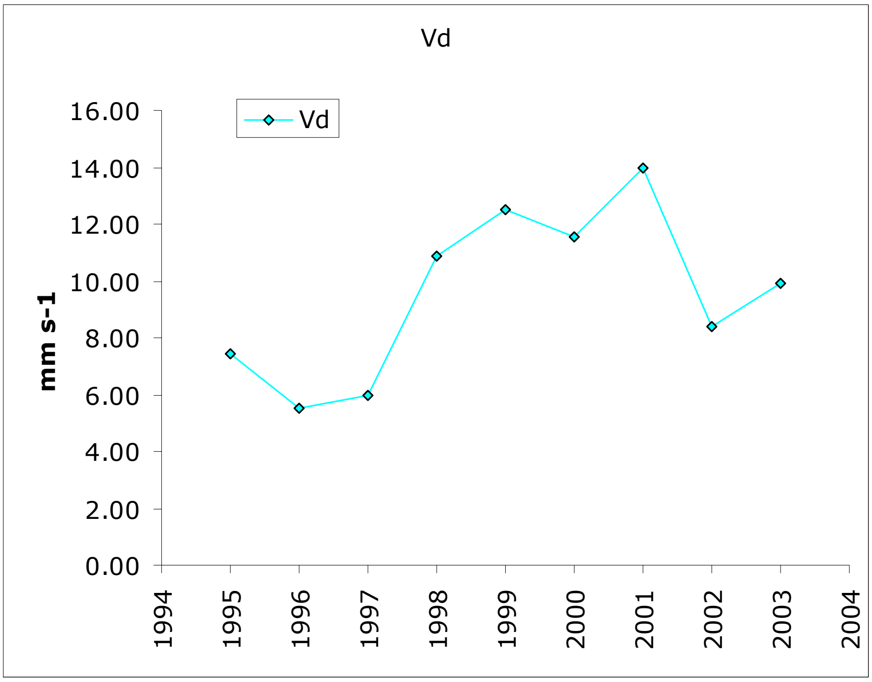


Figure 3.4. Changes in SO_2 deposition velocity with time at Sutton Bonnington between 1995 and 2003

The increase in deposition velocity with time is substantial, especially when compared with the early values, obtained in an atmosphere containing very large SO_2 concentrations and in which the lack of acid neutralizing species maintained a very high acidity in the surface layers and reduced the dissolution of SO_2 at the surface and slowed the deposition process.

3.1. Auchencorth Moss

This moorland site in the Scottish Borders, while at modest altitude (300m asl) is typical of much of upland Britain both in physical and chemical climate and surface vegetation. The site is windy, cool and exposed, but with moderate precipitation (1000 mm). Concentrations of the primary pollutants, like most of upland Britain are small, with SO_2 concentrations below 1ug SO_2 m^{-3} and declining between 1995 and 2001 from 0.6 ug m^{-3} to 0.4 ug m^{-3} as shown in Figure 3.5.

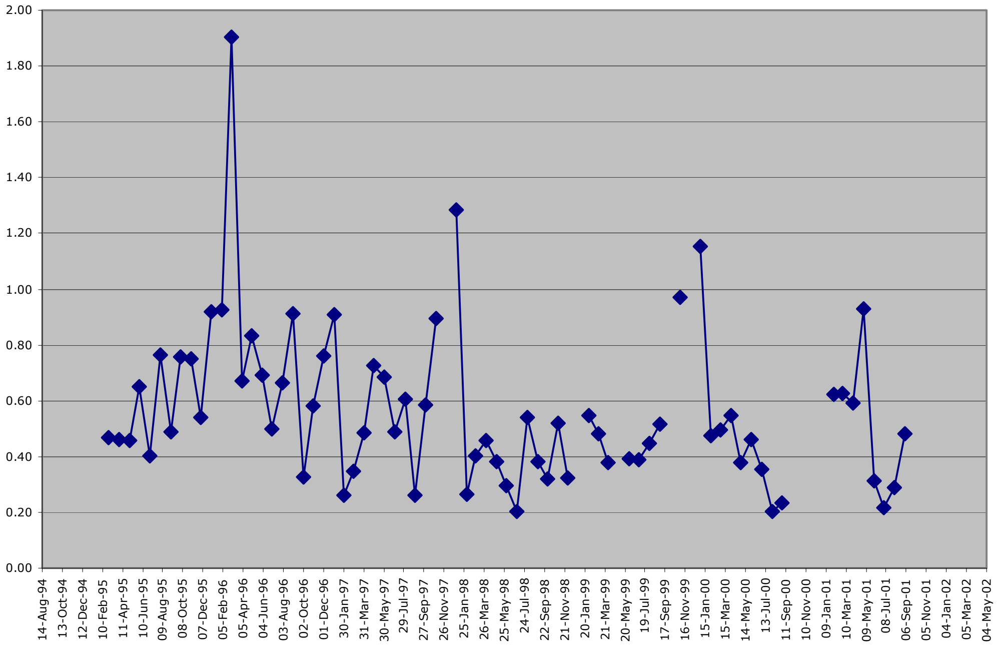


Figure 3.5 The change with time in SO_2 concentration at Auchencorth Moss between 1995 and 2003

The micrometeorological measurements of SO_2 flux have continued throughout the contract and now provide along with the Sutton Bonnington data the longest continuous series of flux measurements for SO_2 globally. It has been a surprise that the rate of deposition would change so much with time, but is consistent with current understanding of the deposition process. The main features of the long-term trend are revealed in the table of annual statistics (Table 3.1)

Table 3.1. Annual statistics of the dry deposition of SO_2 at Auchencorth Moss

	1995	1996	1997	1998	1999	2000	2001
Ra{1m.} (s m^{-1})	34.88	34.25	34.06	31.29	31.38	14.93	31.03
SO_2{1m} (ug S m^{-3})	0.55	0.73	0.52	0.36	0.45	0.39	0.44
$VdSO_2${1m} (m s^{-1})	4.85	4.58	6.00	6.72	5.52	6.47	6.34
SO_2 flux (ng S m^{-2} s^{-1})	-2.74	-3.39	-3.38	-2.70	-2.76	-2.90	-3.01
Rc SO_2 (s m^{-1})	141.77	149.63	101.09	88.50	125.20	98.25	95.59
Rb SO_2 (s m^{-1})	18.41	18.75	18.92	16.91	16.08	28.82	18.05
Vd (mm s^{-1})	4.97	4.67	6.52	7.59	6.11	7.51	6.72
Vdmax	18.76	18.87	18.88	20.75	21.44	22.86	20.40
Rc	147.88	161.02	100.39	83.60	163.51	89.42	99.85

The fluxes are very small, averaging 3ng m^{-2} s^{-1}, the –ve sign simply denotes deposition since by convention a flux toward the surface is –ve. It is notable that the mean annual flux does not change with time even though the SO_2 concentration declines through the period. The reason for the flux remaining approximately constant is that the deposition velocity increases with time, from 4 mm s^{-1} in 1995 to 6 mm s^{-1} in 2001. As the more time resolved data in Figure 3.6 shows, the deposition velocity changes with time are subject to considerable noise and the annual statistics hide much of this variability. However, the trend towards larger values in recent year is clear in the data.

The components of the deposition process necessary to examine the underlying causes may be separated into atmospheric and surface parts. In the case of the atmospheric components, the aerodynamic and boundary layer resistances, these are included in the tabulated annual averages, (Table 3.1). These show interannual variability in the atmospheric resistances (r_a and r_b) but no monotonic trend.

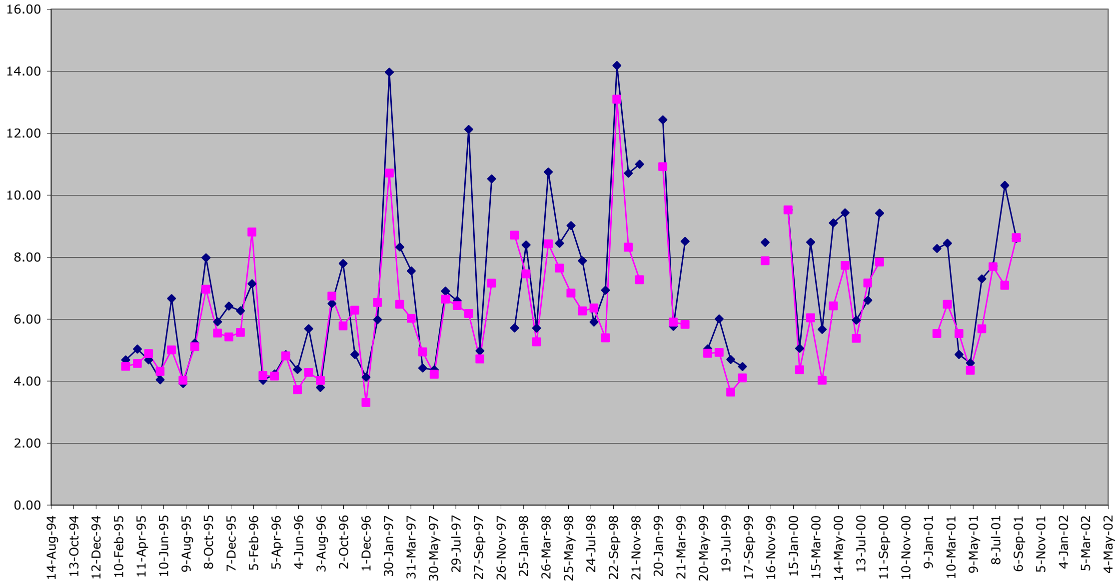


Figure 3.6 Changes in the deposition velocity of SO_2 with time at Auchencorth Moss

The change in deposition velocity with time is large and while consistent with our understanding of the process, the detailed explanation requires sites with concurrent flux measurements of NH_3 and SO_2 (Flechard et al 1997).

The underlying cause of the trend in deposition velocity is the continuing decline in the ratio SO_2/NH_3 which regulates the canopy resistance (r_c). The measurements of canopy resistance at Auchencorth Moss are shown in Table 3.1 and Figure 3.7. The annual statistics in Table 3.1 show a reduction in canopy resistance of about 30% over the monitoring period and is the main reason for the steady increase in deposition velocity. Measurements of monthly mean NH_3 concentration at Sutton Bonnington and Auchencorth Moss throughout the monitoring period show fairly constant concentrations of NH_3 at 4 .5 ug m^{-3} and 0.8 ug m^{-3} respectively throughout the monitoring period, so the trend in the ratio SO_2/NH_3 at the two monitoring sites is driven primarily by the declining SO_2 concentration.

Table 3.2. Concentrations (ppbV) and ratio of ammonia and sulphur dioxide

		1997	1998	1999	2000	2001	2002
Auchencorth Moss	NH_3	1.4	1.1	1.2	0.9	1.0	1.0
	SO_2	0.4	0.3	0.3	0.3	0.3	
	SO_2/NH_3	0.3	0.3	0.3	0.3	0.3	
Sutton Bonnington	NH_3	8.7	6.4	6.9	6.9	7.4	6.3
	SO_2	2.8	2.9	1.7	1.4	1.2	1.4
	SO_2/NH_3	0.3	0.4	0.2	0.2	0.2	0.2

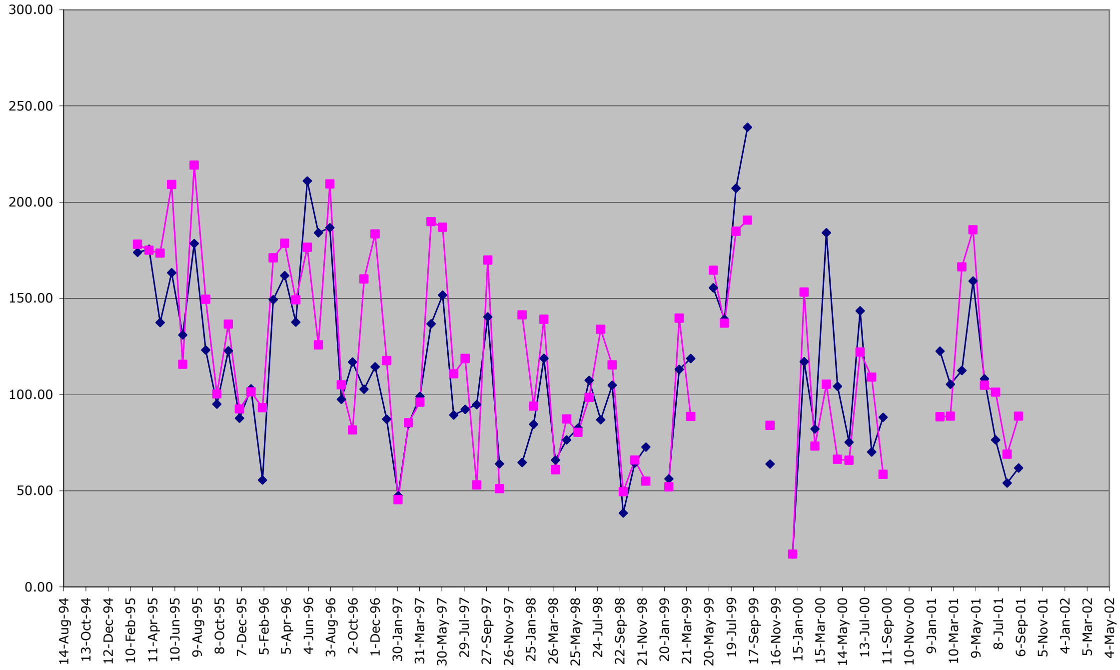


Figure 3.7. Changes with time in the canopy resistance (r_c) at Auchencorth Moss between 1995 and 2001

Acid Deposition Processes:
Mapping Methodology and Deposition Maps

EPG 1/3/166

Rognvald I Smith, David Fowler, Mhairi Coyle, Mark Sutton, Neil Cape, Eiko Nemitz and Jennifer Muller

Centre for Ecology and Hydrology
(Edinburgh Research Station)
Bush Estate, Penicuik,
Midlothian, EH26 0QB, UK.

Mapping Methodology and Deposition Maps

- Deposition maps of acidity, sulphur, nitrogen (oxidized and reduced) and base cations have been produced for the period 1998-2000, including significant new methodologies and data for calculation of critical loads and levels.

This Chapter starts with an overview of the general mapping procedure and methodology. This is followed by a section on the latest changes in mapping including an assessment of implications and comparison of maps . A more in depth description and discussion of the wet, cloud and dry mapping procedure (from measurement to map) is being provided in the Annex.

4. MAPPING METHODOLOGY AND DEPOSITION MAPS

4.1 Deposition of air pollutants to the UK landscape

4.1.1. OVERVIEW OF THE ESTIMATION PROCEDURE

The process of removing air pollutants from the atmosphere and depositing them onto ecosystems can be split into three pathways, each modelled separately.

Dry deposition is the direct removal of the pollutant gas to vegetation, soils or other surfaces. Wet deposition is incorporation of the pollutant into water droplets which are then removed in rain or snow. Cloud droplet or particulate aerosol deposition occurs when either small water droplets or particles are removed by landing directly on surfaces. The combination of these processes provides the (total) deposition of the pollutant, the quantity used in the critical load exceedance calculations.

For the purposes of calculating critical loads, air or rain concentrations of pollutants are mapped from observational data collected through the year, primarily by the UK Acid Deposition monitoring networks (see the Web site http://www.airquality.co.uk/archive/nonauto.php for data). The initial concentration maps are produced by interpolation between the monitoring sites, usually by a technique called kriging. For some of the gases (SO_2, NO_2 and NH_3), there is extra information on local variability which is added to the interpolated map to increase the concentration close to known sources of the gas. For SO_2 the sources are associated with urban areas, for NO_2 the major extra component is from road traffic and for NH_3 the pattern of high and low concentrations is associated with the agricultural activity within the landscape. Ion concentrations of pollutants in rainfall also vary at a similar scale (of the order of 1 km) across the landscape. As this variability is associated with rainfall amount, the adaptation of the concentration map is not done explicitly but is included within the wet deposition model.

The dry deposition model simulates the transport of gas molecules from the atmosphere directly onto a surface, such as the soil surface or a leaf surface, or into plants through stomatal uptake. A number of processes control this exchange, and rates of deposition are dependent on both the turbulence of the atmosphere and the properties of the surface. For SO_2, for example, the current model requires hourly meteorological data on the wind speed, solar radiation, temperature, and vapour pressure deficit (ideally at 1m to 3m above the canopy surface) as well as vegetation data on canopy height and surface roughness, rates of molecular diffusion close to the vegetation surfaces, parameters to control stomatal opening for the particular species of plant, and the stage of plant development within the growing season including its current leaf area index.

Wet deposition is a simple product of rainfall amount and rain ion concentration, when both measurements are available and the landscape is flat. However in undulating landscapes more typical of the UK, rain ion concentrations in frontal rain (the most common form of rainfall) are increased on higher ground by the gathering of extra pollutant within clouds - typically visible as cap clouds on hilltops. Therefore higher altitude sites experience both increased rainfall amount and increased pollutant concentration in rain, and unfortunately there is no simple relationship with altitude to model this effect. The effect is modelled using the ratios of ion concentrations measured in cloud and in rainfall along with an estimate of the extra rainfall amount caused by proximity to the hills.

Aerosol particle and cloud droplet deposition is modelled in a similar manner to the first stage of the dry deposition model, with turbulence, estimated from wind speed and vegetation surface roughness, controlling the delivery of pollutant to the atmosphere close to the surface. For cloud droplets, the process is then controlled by momentum but for aerosol particles in smaller size ranges there remains some debate as to the appropriate removal rates to use for different particles sizes and different types of vegetation.

Further information on the above models and their implementation, including some discussion of relevant issues and further references, is available in RGAR (1997), NEGTAP (2001), Smith and Fowler (2001), Smith et al (2001) and Smith et al (1997).

4.1.2. IMPORTANCE OF THE DIFFERENT PATHWAYS AND INTERPRETATION OF THE ESTIMATES

In terms of importance, wet deposition dominates inputs to the high ground and most of the west of the UK with dry deposition of increasing importance in eastern areas. Cloud droplet deposition is only of major importance for forest ecosystems in the more eastern hill areas of the UK and, at least until recently, particle deposition was substantially less than dry deposition. The present deposition estimates for critical loads do not include particle deposition, and it is expected that estimated total deposition will be increased slightly in the future by inclusion of this process (+10 to 15 %).

Scale

Clearly even the meteorological data required by the above models to estimate the deposition to any specific ecosystem in the UK are not available at the required spatial scale. Also there is very little information available on the plant parameters required by the models except for a very limited number of plant species, mainly the relatively common agricultural species. Therefore generalisations are used to estimate uptake to typical broad ecosystems within an area. Only 5 land use categories - arable, forest, grassland, moorland and urban area - are used to determine the vegetation characteristics for the models. The models calculate average and land use specific deposition to 5 km x 5 km squares across the UK, where the average deposition is the calculated using the percentages of the 5 km x 5 km square assigned to each of the 5 land use categories. Although formally assigned to a specific geographic location, the interpretation of the deposition value is that this is the best estimate of expected deposition to a particular ecosystem type (in terms of approximate altitude and vegetation composition) somewhere in the region. Although not explicitly defined, the size of that region should be considered to be about 50 km x 50 km. Likewise to avoid the year to year variability in meteorology with some very dry and some very wet years, the deposition for critical load exceedance is calculated as an average deposition over a three year period.

Uncertainty

Assessment of the uncertainty of a deposition estimate at the 5 km x 5 km scale is a continuing task. There are some pointers which may be helpful pending a more complete assessment. Sulphur deposition is better estimated than nitrogen deposition, as it is less variable spatially and it is easier to track through an ecosystem, so the estimates of deposition can be more fully checked through catchment studies. Nitrogen is much more reactive within the landscape, with many more sources, and it cannot, generally, be tracked through an ecosystem. Analysis of the wet deposition model suggested a level of uncertainty of ±20% for sulphur at best and this would be substantially increased for nitrogen. The output from the dry deposition model is definitely less certain, with optimistic values of ±50% more likely from an uncertainty analysis. Where data on measured dry deposition are available, they indicate that even these estimates are probably too optimistic, with the models and measurements often only coming within a factor of 2 or 3. Therefore, a subjective assessment suggests that a 95% confidence band around the deposition estimate for a critical load exceedance calculation on a chosen 5 km x 5 km square of ±30% is probably over optimistic, ±50% is optimistic and ±100% is quite likely.

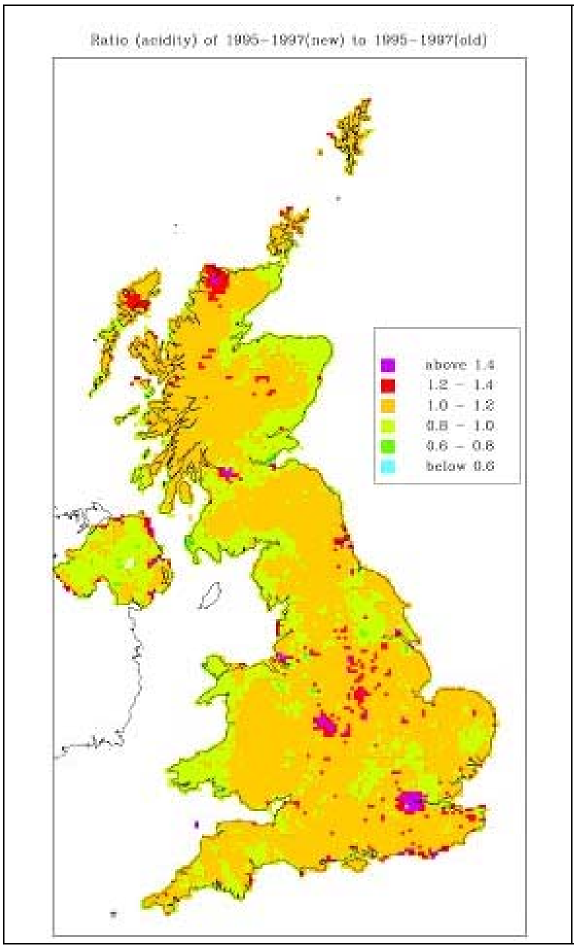
4.1.3. CHANGES IN PROCEDURES OVER TIME

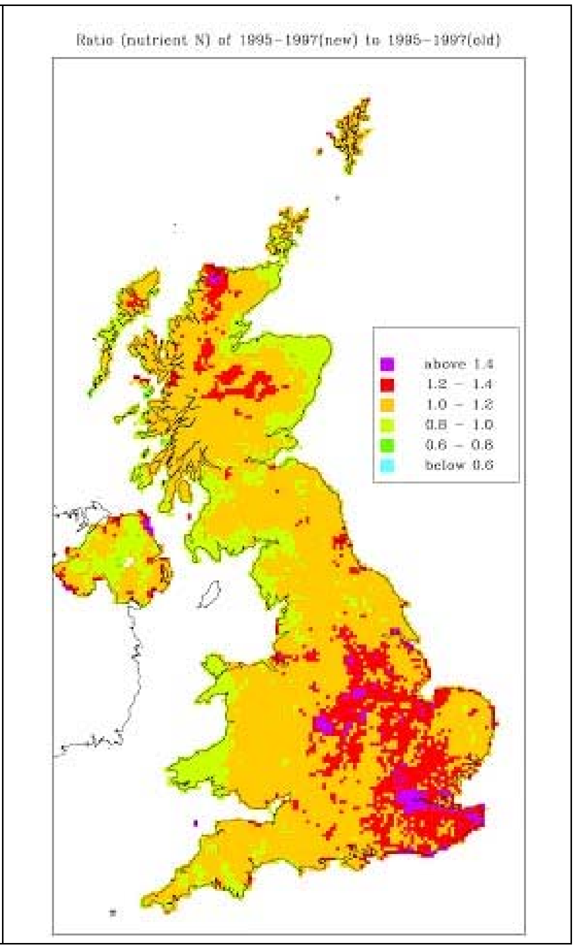
There have been a large number of changes since these models were first used to estimate deposition for critical loads for the period 1995-1997, to include or improve process descriptions and manage new data. Most of these have not had a substantial effect on the estimated deposition totals for the country but have changed the spatial distribution. Examples of these changes include an improved land use classification, improvements in interpolating the meteorological inputs, use of a new rainfall field implemented at the UK Meteorological Office, revision of the wet surface uptake parameterisation of SO_2, and a different calculation of the effect of urban sources of SO_2.

One important change was the inclusion of deposition of nitric acid, now possible since the establishment of the nitric acid monitoring network, with data available since 1999. In UK terms, nitric acid deposition accounts for 30% of the deposition of oxidised nitrogen with the deposition is highest in England, particularly towards the southeast.

The other change which has been important was a revision of the method used to produce the NH_3 concentration map. A major part of the variability in NH_3 concentration is provided by the output from an atmospheric transport model (FRAME), since the local scale variability in NH_3 emissions is a major cause of changes in concentration. The NH_3 monitoring network started in mid 1997 and there were therefore few data to cover the period 1995-1997, so the modelled concentrations were the primary data source. With the accumulated evidence from a network of approximately 100 sites of the concentration field for NH3, it has become clear since then that an adjustment is required to bring together the measurements from the NH_3 monitoring network and the model output concentrations, and this adjustment is now in place. The adjustment (calibration) procedure provides the grid square average NH_3 concentration and therefore underestimates concentrations very close to major sources. As NH_3 concentrations drop substantially within 1 km of a source, this concentration is appropriate for most of the 25 km^2 in a 5 km x 5 km square. However there will be areas within many UK 5 km x 5 km squares where the NH_3 concentration, and hence nitrogen deposition, is substantially underestimated by using this typical value for the whole of the 5 km x 5 km square. This can only be resolved by either introducing more local concentration monitoring or running a local scale model within the 5 km x 5 km square.

To separate the changes due to changes in the model rather than by changes over time, maps of deposition for 1995-1997 using the current models have been provided. The ratio comparison of 1995-1997(new) deposition against 1995-1997(old) deposition for total acidity and nutrient N are shown to indicate where changes have resulted from improvements to the models. Therefore the 1995-1997(new) acidity and nutrient N depositions include nitric acid deposition from 2000 as an initial step towards correcting for the omission of nitric acid in the 1995-1997(old) data. The ratio comparisons of 1999-2001 with 1995-1997 using the current models are then shown to indicate the changes with time. For this comparison, the acidity deposition is not adjusted for deposition of non-marine base cations or chloride, so is just the sum of sulphur and nitrogen inputs. The adjustments for non-marine base cations or chloride are relatively small and the estimated deposition for the 1995-1997 period is rather uncertain.





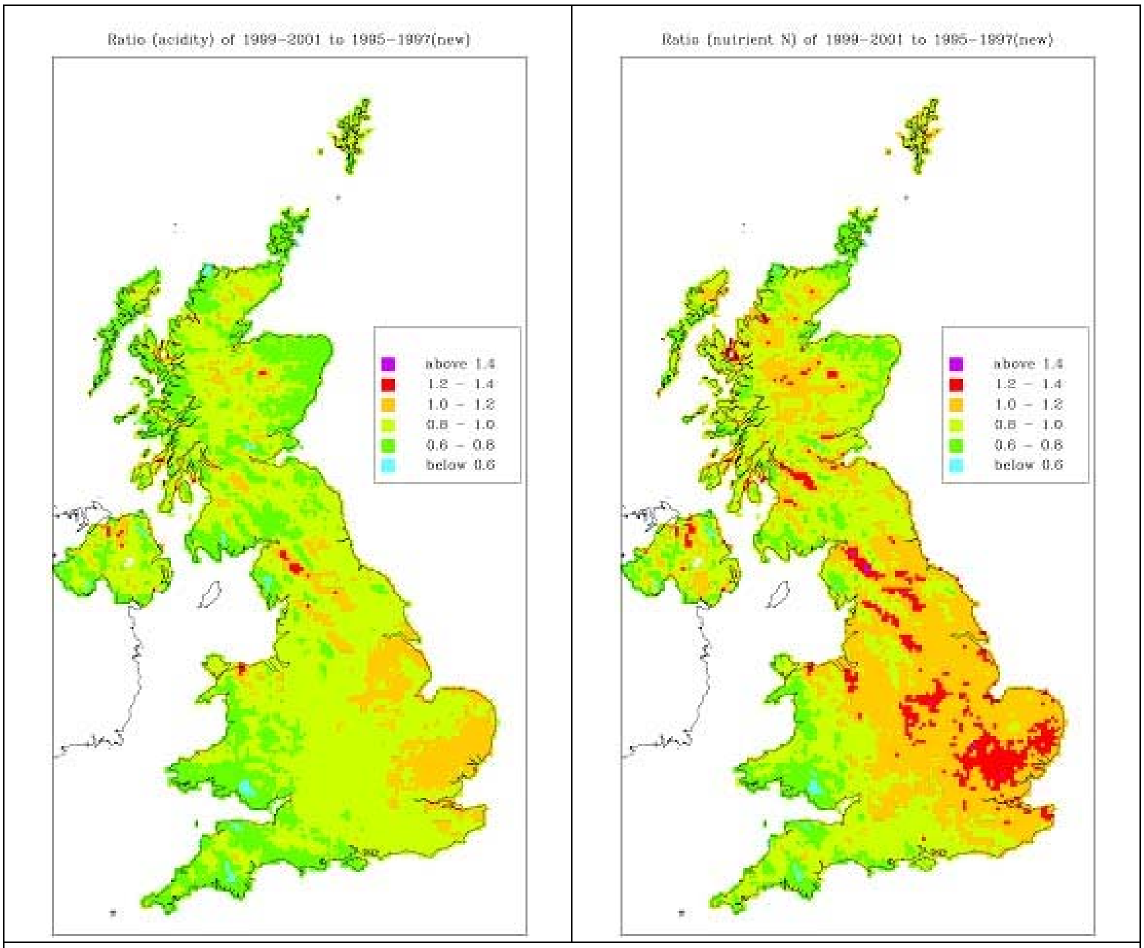


Figure 4.1. Comparison of model differences (1995-1997(new)/1995-1997(old), first Panel) and of time differences (1999-2001/1995-1997 , second panel) for acidity(*) and nutrient nitrogen deposition.(*) the acidity deposition is not adjusted for deposition of non-marine base cations or chloride

The comparison between the old and new models for 1995-1997 acidity deposition shows most areas reporting changes of less than 20%, and the main increases outside that range appear to be associated with urban areas. The acidity map does highlight an improvement in the method of estimating the extra rainfall over hills, which has affected the mountain areas in the Outer Hebrides and the very northwest of the Scottish mainland on either side of the Minch. The newer method should be more consistent when there are major offshore islands, as in this case. The increases in nutrient N deposition are primarily a reflection of the inclusion of nitric acid deposition, although changes over most of the country are again less than 20%. The main areas of increase are, as expected, in England. The increased deposition of nutrient N in the Scottish mountain areas is a combination of the above change in estimation of wet deposition along with an assumed very rapid rate of deposition of nitric acid, even at low concentration, to forests.

The temporal change in acidity deposition reflects the general decrease associated with sulphur deposition at the end of the 1990s. Where there are increases, these are more clearly visible in the temporal change in nutrient N deposition. There was a general increase in nitrogen deposition in 2001 compared to 2000, with nitric acid deposition showing a particular increase. The increases of over 20% on the map of temporal change in nutrient N do not appear to be from a single cause although those towards the southeast of England are more associated with nitric acid than the other components. In summary, the deposition of acidity has picked up the improvement with lower sulphur deposition, but the changes in nutrient N over the period show substantial areas of the country with an increase in deposition.

4.1.4. SUMMARY

Estimated deposition of acidity, N and S in the UK rely on a comparison of extensive networks of measured concentrations of the key gases and solutes in rain to underpin the mapping process. The process-based models used to calculate input to the surface are state of the art and are tested routinely against measurements. Thus the UK is provided with estimates of deposition which can be regarded to be as good as any in Europe and better than most. However uncertainty in the mapped values are limited by the spatial distribution of the estimates (5x5km) and by uncertainties in the understanding of the process and components not included (e.g. aerosol deposition).

The current estimates of nitrogen deposition will increase with the future addition of aerosol deposition especially for aerodynamic surfaces. Close to sources of ammonia (NH_3) the deposition is likely to be an underestimate of the nitrogen input to an ecosystem and additional local scale modelling is desirable.

The inclusion of nitric acid deposition has been a major change from previous estimates, primarily affecting England but also increasing nitrogen deposition to forests over most of the UK.

The expected reduction in acidity with reduction in sulphur emissions is clear throughout the UK.

The changes in N deposition are small in the UK totals, but significant changes in the spatial pattern of N deposition due to primary improvements in the calculation procedure over 5 years are evident.

4.2. Changes in mapping methodology and implications

4.2.1. MAR04-VERSION AND RESULTING CHANGES

A new version (Mar04) of the mapping procedure has been produced to provide a consistent methodology. This should make tracing of any subsequent changes much easier and is an improvement on all previous versions.

For example, the procedures for producing the seeder-feeder enhancement to wet deposition are now consistent whether or not rainfall for Northern Ireland was supplied by the Met Office for a particular year. Previously the enhancement was calculated from the supplied rainfall map, which has been quite different in coverage over the period, and which did result in difficulties in understanding differences between years in some areas of the wet deposition maps. The new procedure starts by first extending the Met Office map to cover the whole UK domain.

This version is the baseline version from which it will be moved on and to which comparisons will be provided.

The differences with the new version are likely to be most apparent when the data are used regionally or for local area decisions.

The 'Mar04' version is one that can be documented not only for the recent years, but for the whole period since 1986, it can be subject to quality control and it should provide the confidence that is required.

Base comparative studies should be done with the 'Mar04' data as the baseline to enable better progress.

The deposition outputs of 'Version Mar04' that are available are

- wet and cloud deposition 1986-2001 (Ca & Mg missing 1992-1999, H missing 2000)
- SO_2 1987-2001
- NO_2 1996-2001
- NH_3 1996 and 1999
- HNO_3 2000-2002

and critical loads values are now available as

- 1995-1997 (using new SO_2 interpolations, calibrated NH_3 for 1996, average Ca and Mg from 1991 and 2001, HNO_3 for 2000)
- 1998-2001 (using new SO_2 interpolations, calibrated NH_3 for 1999, Ca and Mg from 2000 only, average H from 1998 and 1999, HNO_3 from 2000)
- 1999-2001 (using new SO2 interpolations, calibrated NH_3 for 1999, average Ca and Mg from 2000 & 2001, average H from 1999 & 2001, average HNO_3 from 2000 and 2001)

There are changes in Version Mar04 critical loads data from the previous data sets, with the major ones as follows:

(a) the previous 1995-1997 had older concentration map interpolations, no HNO_3, uncalibrated NH_3 for 1996 and a different seeder-feeder rainfall procedure;

(b) the 1998-2000 (version 3) had a first version of the 1999 NH_3 calibration some minor differences with interpolated concentrations, and a different seeder-feeder rainfall procedure.

4.2.2. CHANGES FROM 95-97 TO 98-00 MAPS

The major points between the two sets of maps is

a) lack of HNO_3 deposition in the 95-97 data – no HNO_3 data were available prior to 2000

b) NH_3 concentration data from the monitoring network (started in mid 1997) were not properly included in the calculation of deposition

c) there was debate which was never properly resolved about the base cations - only since 2000 have data was available to confirm there was a problem during the 1990s

d) cloud droplet deposition was substantially underestimated, but since this is a small quantity this is normally not noticed

4.2.3. HNO_3

There is a nitric acid concentration map available on the web at

http://www.edinburgh.ceh.ac.uk/cara/UKNAMN/uknamn_nit_maps.htm

The deposition of HNO_3 broadly follows the concentration pattern. It is larger over aerodynamic rough surfaces (forests, urban areas), so it is a bigger issue in England than the other countries - but some of the smoothness in that map is a consequence of a relatively small number of monitoring sites. For the 3 years for which observations are available, the budgets (in kt N per year) for England&Wales, Scotland and N. Ireland are presented in Table 5.1.

Table 4.1. UK Nitric acid budget for 2000-2002

	England and Wales	Scotland	N.Ireland
2000	47.80	8.83	0.813
2001	60.07	11.57	1.129
2002	51.08	10.28	0.922

The inclusion of HNO_3 deposition was flagged at least two years ago, i.e. 2002 when it was pointed out that it was likely to be of the order of 3 times NO_2 deposition and that the main effect was likely to be over England. The known changes with oxidised N deposition and the base cation (and non-marine chloride) issues were part of the reason why there were several tests version of the 1998-2000 data. Feedback from users is not to change our science input, but to identify where problems occur and get some feel for how important an assessment of uncertainty is in that particular area. For example, extra runs were done at DEFRA's request to reduce the HNO_3 deposition velocity (particularly to forests) to test the effect on the critical loads - the effect was not large and best estimates of deposition velocity to forests were retained.

4.2.4. CALIBRATION

Calibration of the modelled data and measured fields was introduced during the interpretation of the NEGTAP report (2001) to allow the deposition estimates based on measured concentration fields from past data to be combined with future estimates from long-range transport models (FRAME and HARM), without discontinuities and apparent trends simply due to measurement model differences.

The modelled deposition fields for the UK are now routinely calibrated against measurement based deposition values as described in NEGTAP (2001).

4.2.5. INTERPRETATION OF AMMONIA DEPOSITION

The effect of the NH_3 network locations on the interpretation of the deposition map: Most sites are not beside obvious NH_3 point sources, and so the current deposition doesnot reflecting peak concentrations which may occur in a 5km square near to a point source. Therefore, for planning, etc., if there were a point source then local modelling would be required to add extra concentration to the value from the 'UK map'.

This also implies that critical load exceedances are probably currently slightly underestimated nationally - depending on how many large point sources are next to (i.e. very close to) sensitive ecosystems. This requires further discussion, but this is concerning distances of the order of 1km rather than 5km.

The calibration of NH_3 FRAME concentration maps to the data from the NH_3 monitoring network is the correct way forward at present, but the interpretation of the output is quite important. If there is a strong source of NH_3 emission in a 5km square, then the NH_3 concentrations are elevated very considerably close to the source (say within 1km). However, the majority of the 5km square will not experience these high concentrations, and the sites in the monitoring network are generally placed not immediately close to any sources. Therefore, the deposition maps of NH_3 will reflect the UK situation for areas not beside sources. If these data are to be used in a situation where there is a local substantial source, then the extra NH_3 from that source should be modelled before coming to a conclusion with respect to a critical loads exceedance.

4.2.6. DEPOSITION MAPS

Deposition maps and budgets are presented in this report for 2001 because for 2002, the 5 km x 5km rainfall required to complete wet deposition and cloud is unavailable, for all other species 2002 maps are currently available.

The first three sets of maps compare 95-97 (ORG) with 95-97 (Mar04) i.e. a comparison of methodology/version (Figure 4.2.-4.4.). The second three sets compare 95-97 (Mar04) with 99-01 (Mar04), i.e. deposition changes with time (Figure 4.5.-4.7).

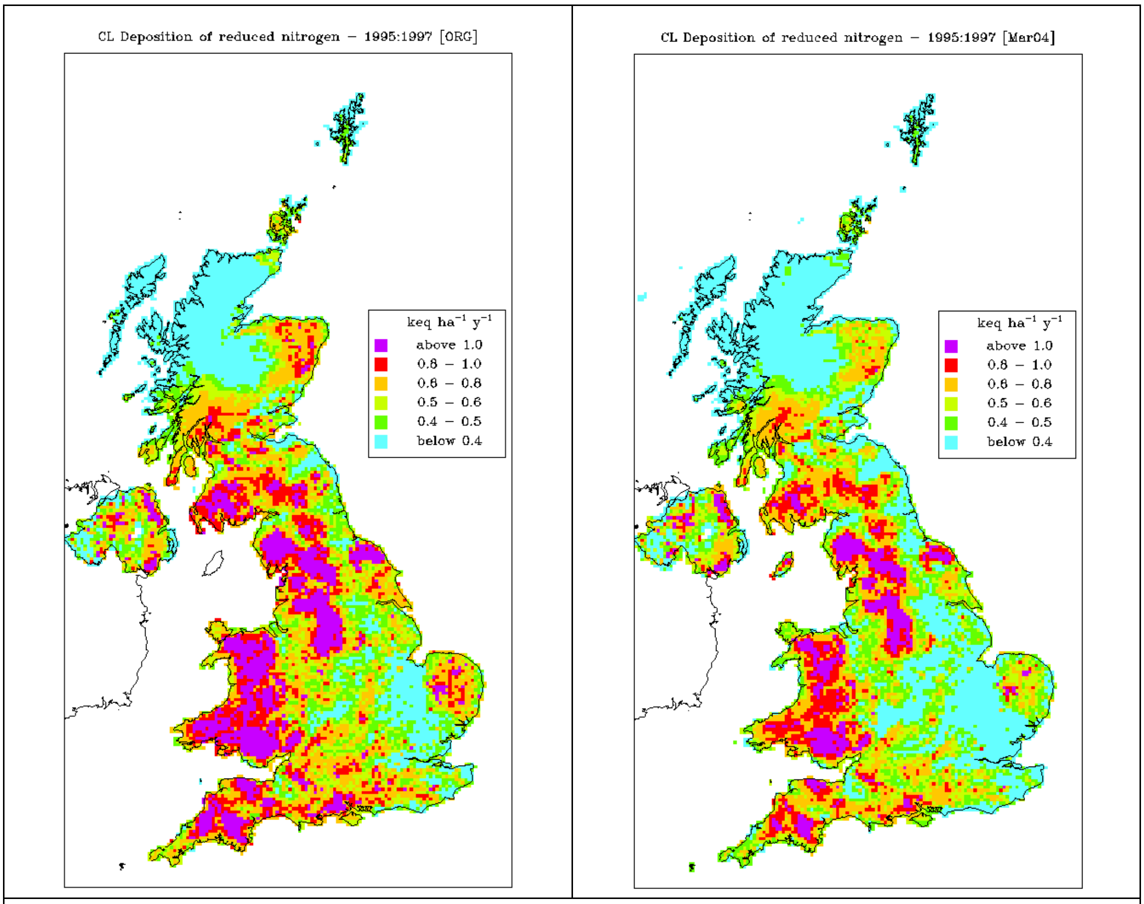


Figure 4.2. Comparison of reduced nitrogen 95-97 [ORG] with 95-97[Mar04]

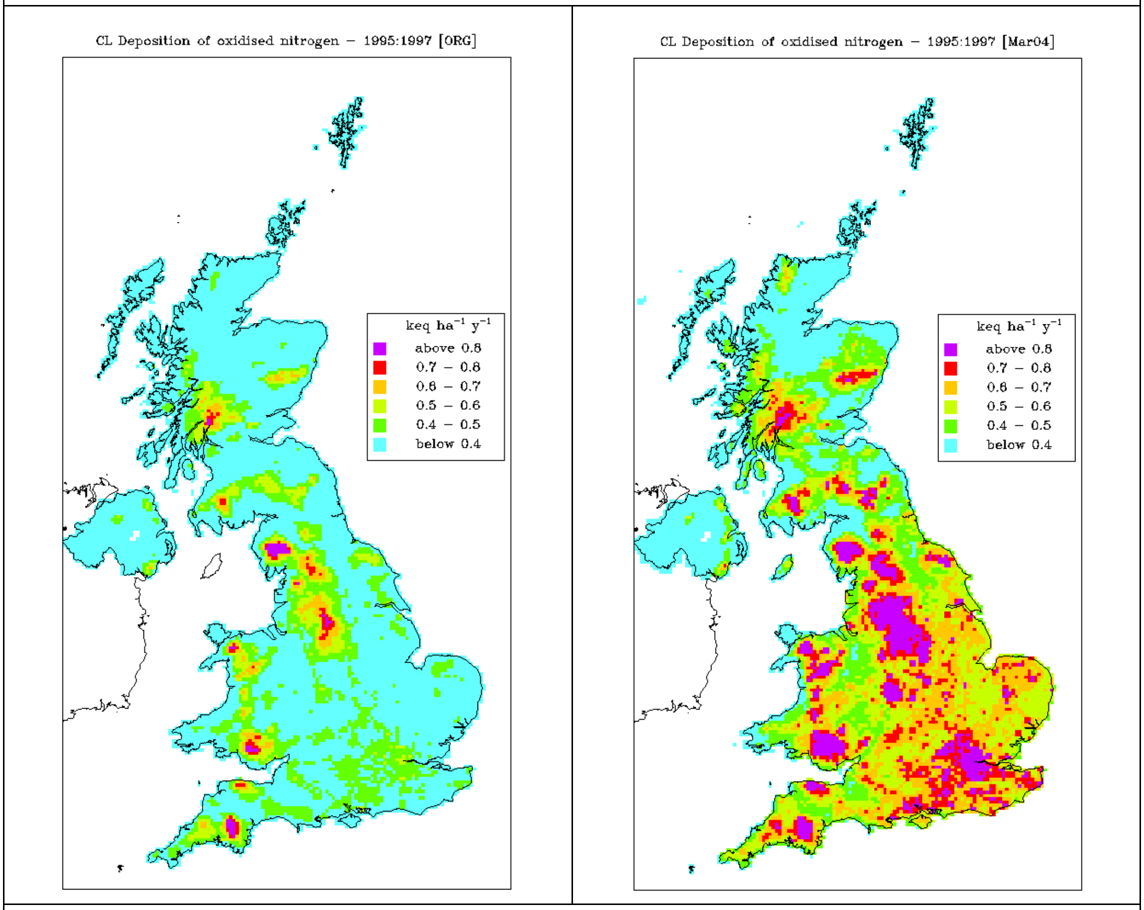


Figure 4.3. Comparison of oxidised nitrogen 95-97 [ORG] with 95-97[Mar04]

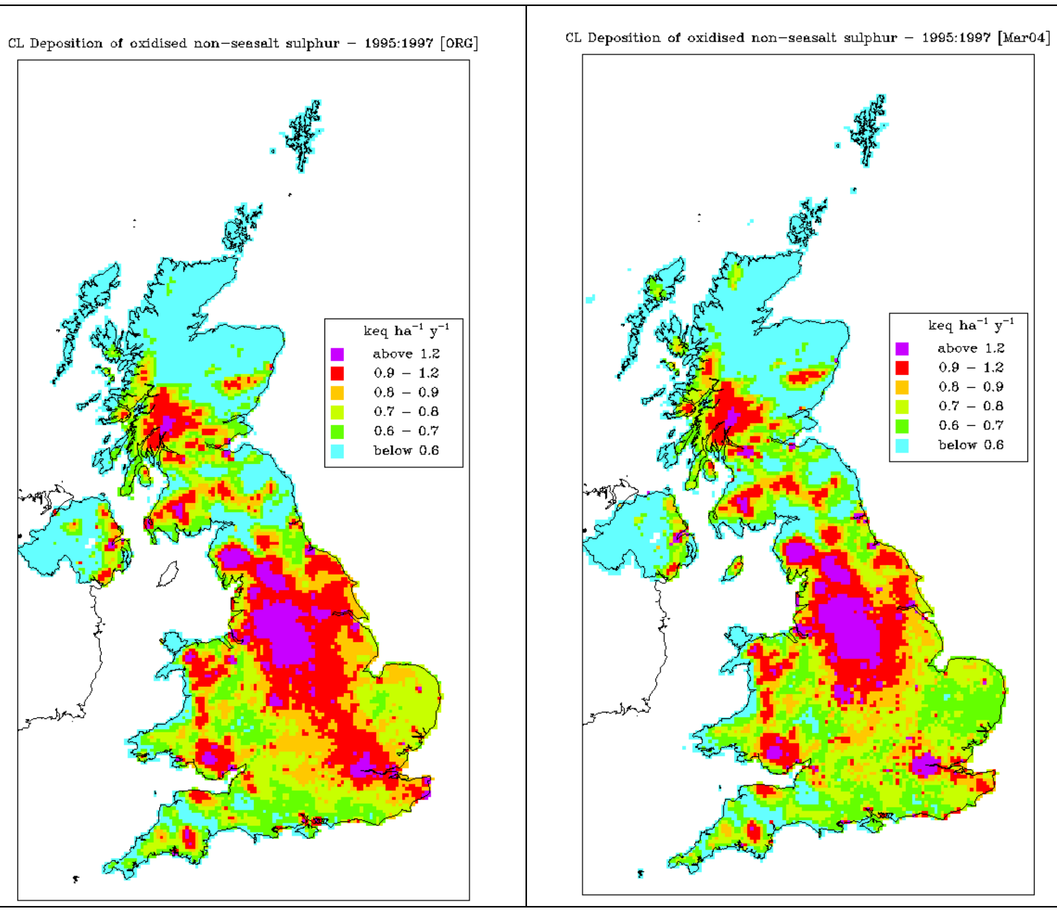


Figure 4.4. Comparison of oxidised non-seasalt sulphur 95-97 [ORG] with 95-97[Mar04]

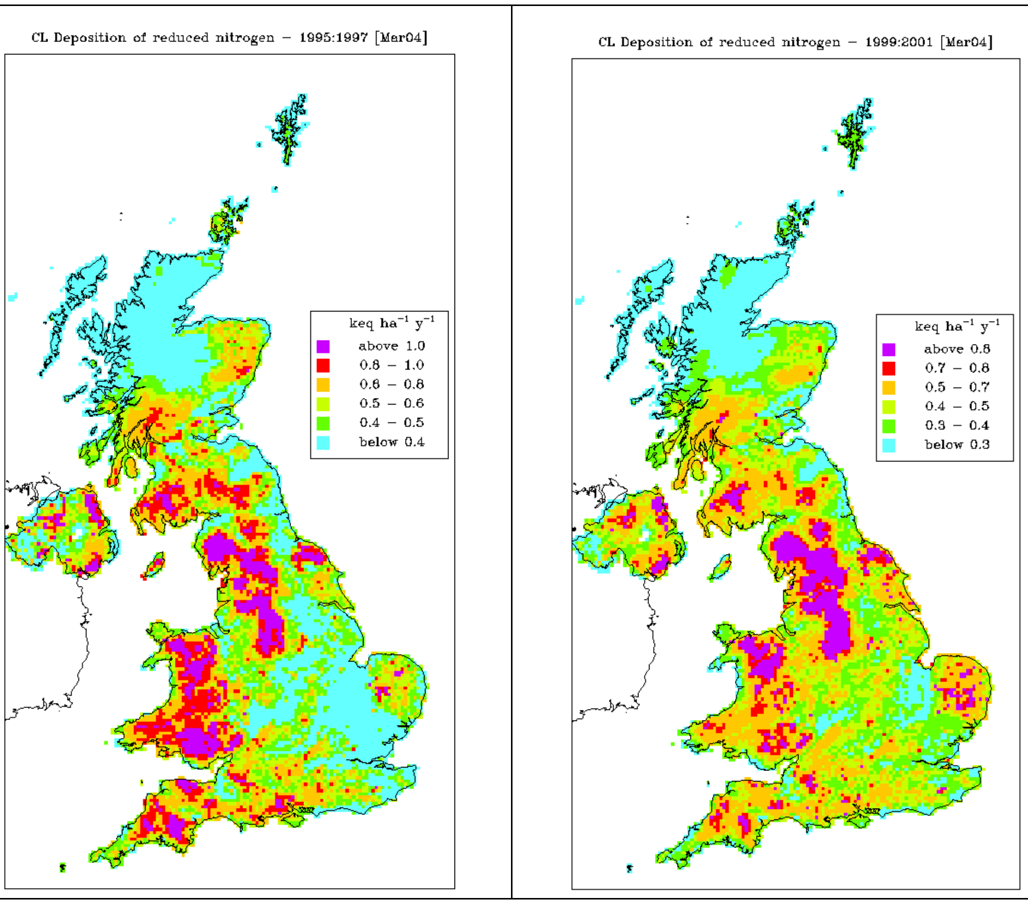


Figure 4.5. Comparison of reduced nitrogen 95-97 [Mar04] and 99-01[Mar04]

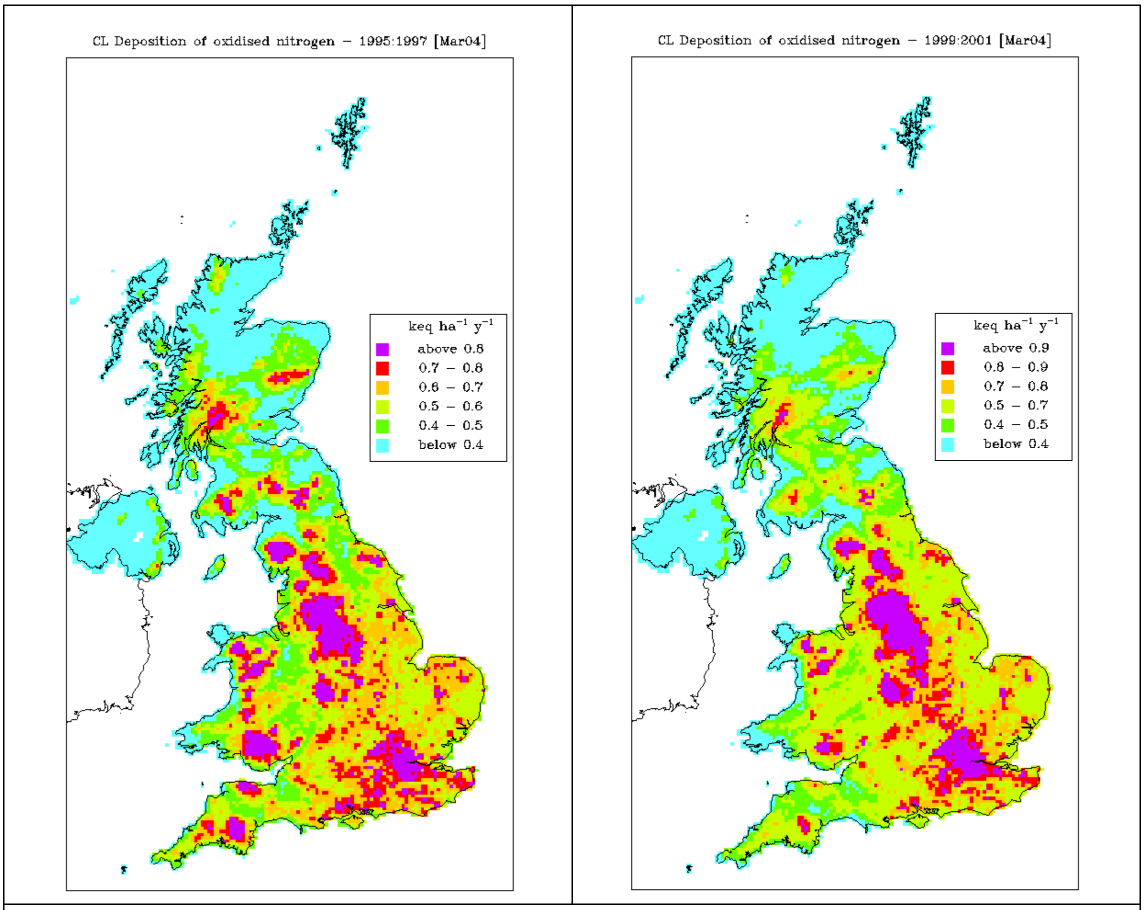


Figure 4.6. Comparison of oxidised nitrogen 95-97 [Mar04] and 99-01[Mar04]

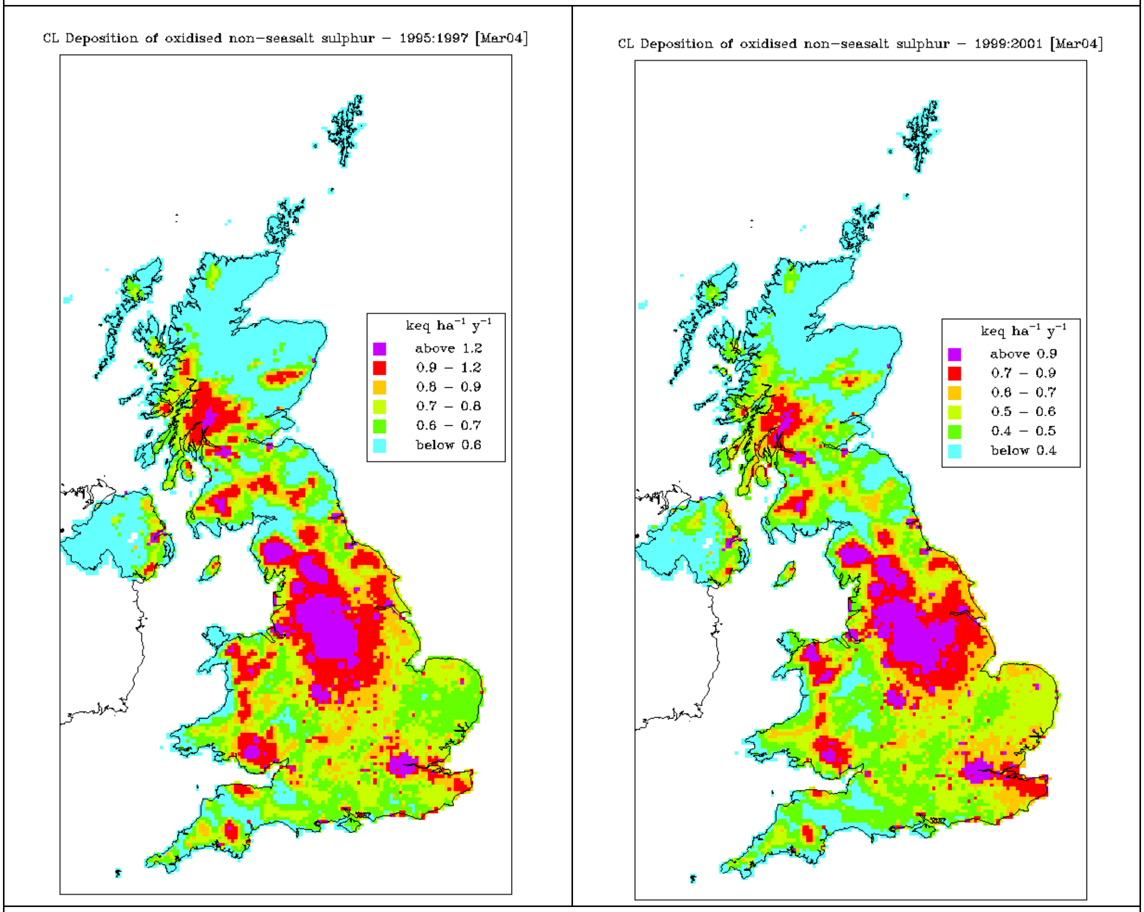


Figure 4.7. Comparison of oxidised non-seasalt sulphur 95-97 [Mar04] and 99-01[Mar04]

4. 3. Deposition Maps

Deposition maps for the UK:

A selection of deposition maps of acidity, sulphur, nitrogen (oxidized and reduced) and base cations have been presented for the period 1998-2000, including significant new methodologies and data for calculation of critical loads and levels.

4.3.1. OXIDISED NITROGEN

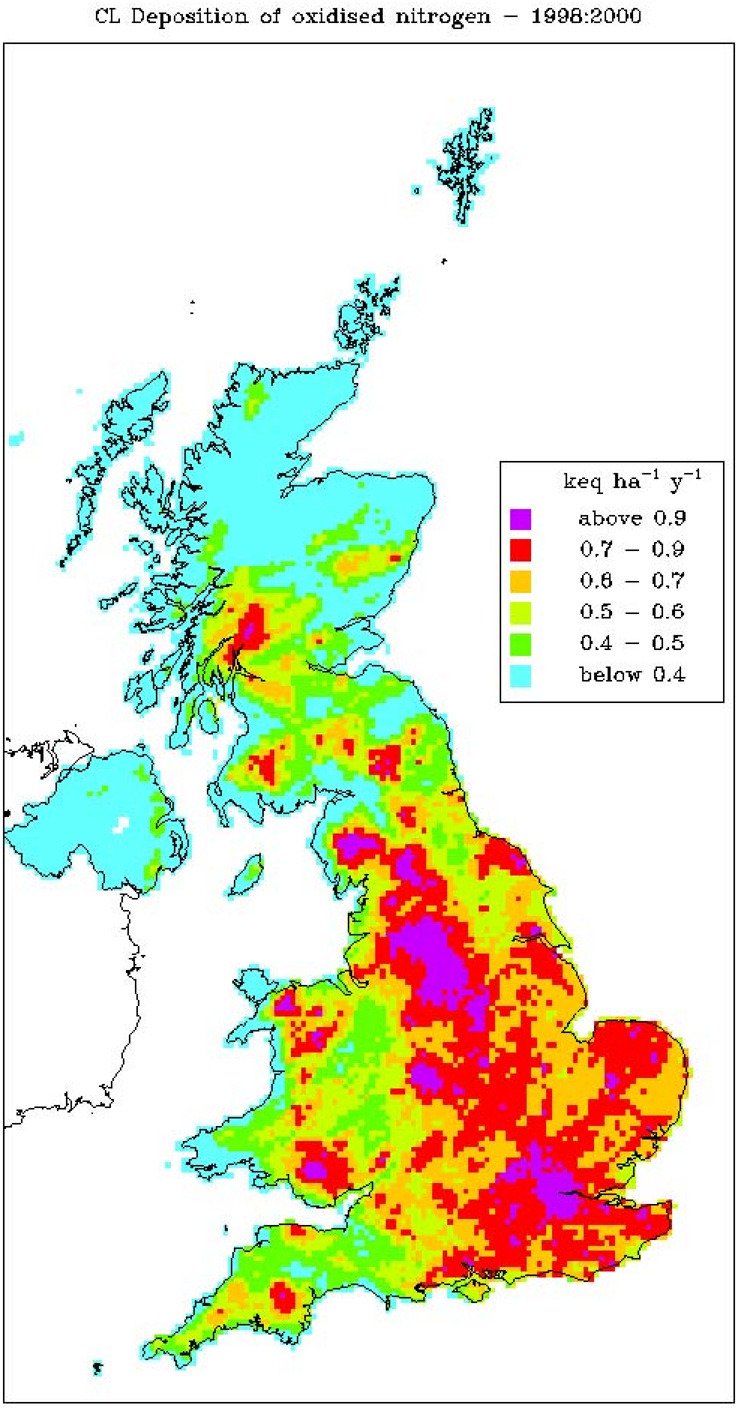


Figure 4.8. Composite oxidised nitrogen deposition 98-00

4.3.2. REDUCED NITROGEN

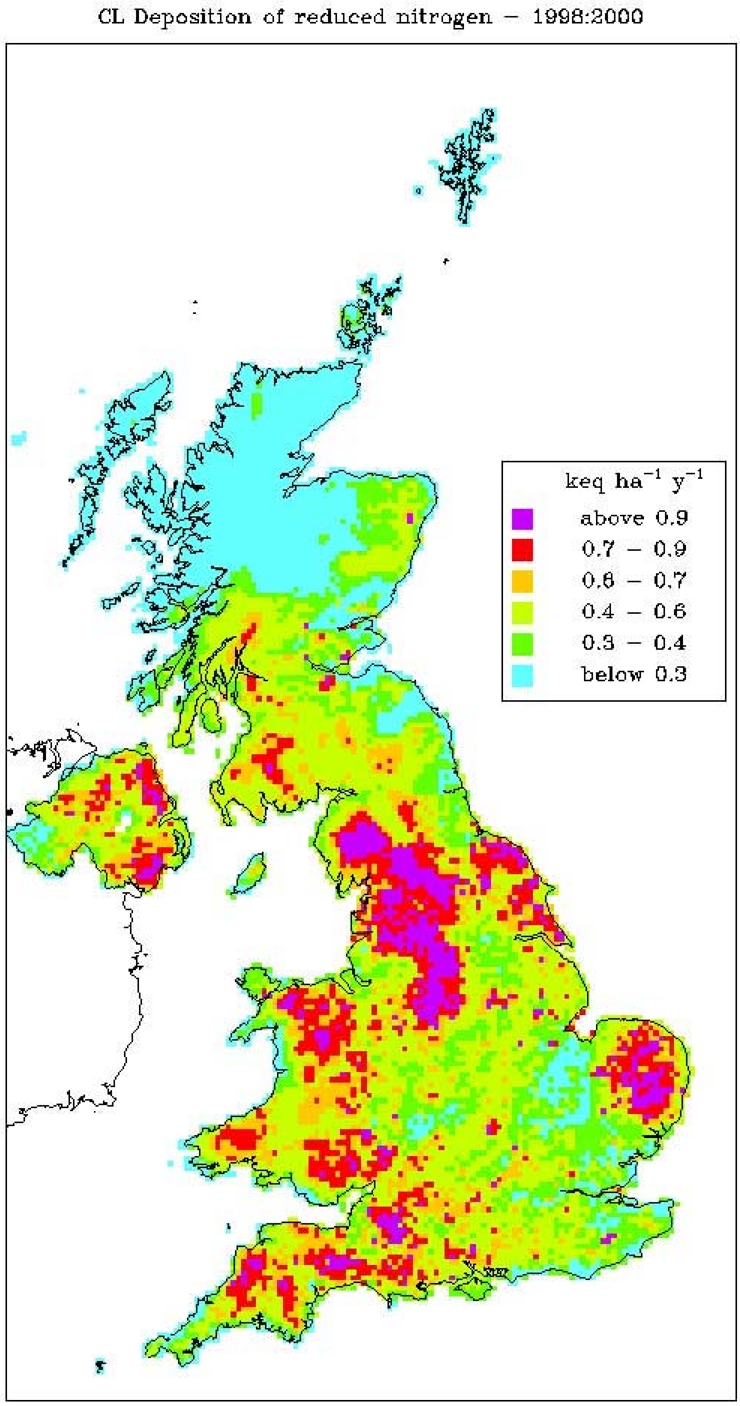


Figure 4.9. Composite reduced nitrogen deposition 98-00

4.3.3. NON-MARINE SULPHUR

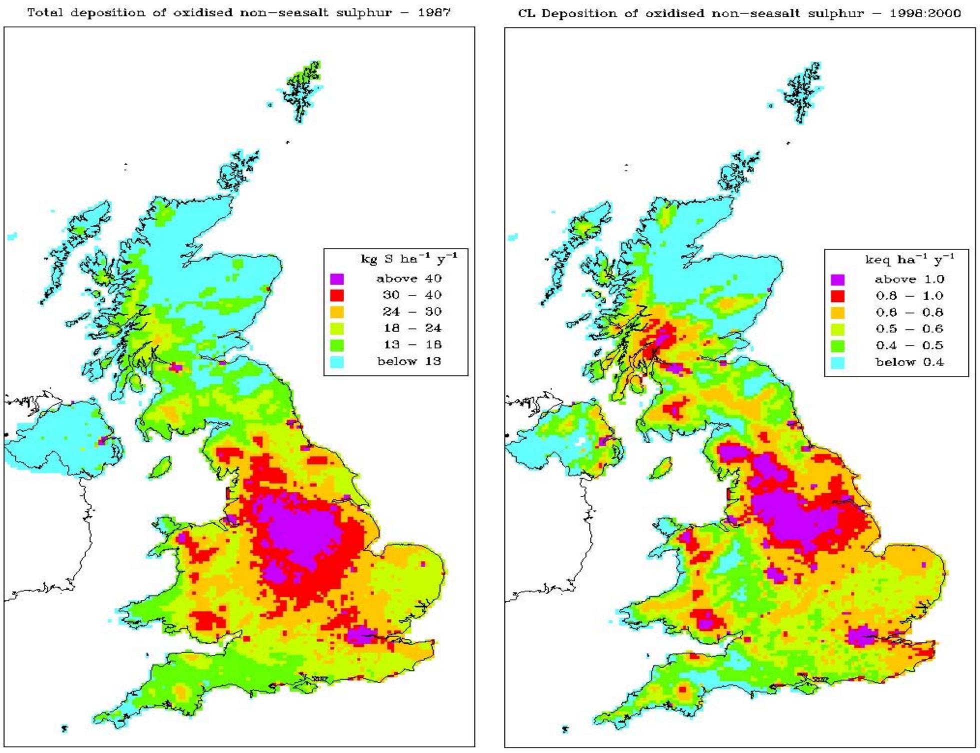


Figure 4.10. Total oxidised non-seasalt sulphur deposition 1987 and composite 98-00

4.3.4. TOTAL BASE CATIONS

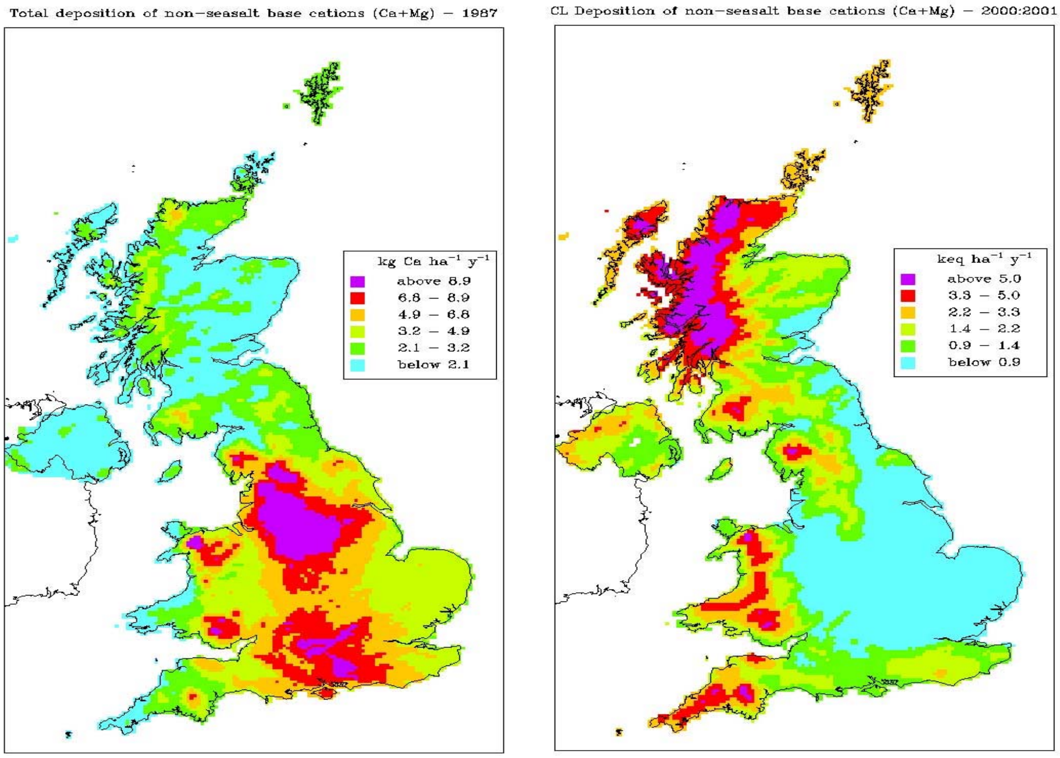


Figure 4.11. Total deposition of non-seasalt base cations (Ca and Mg) 1987 and composite 00-01

4.3.5. TOTAL ACIDIFYING INPUTS

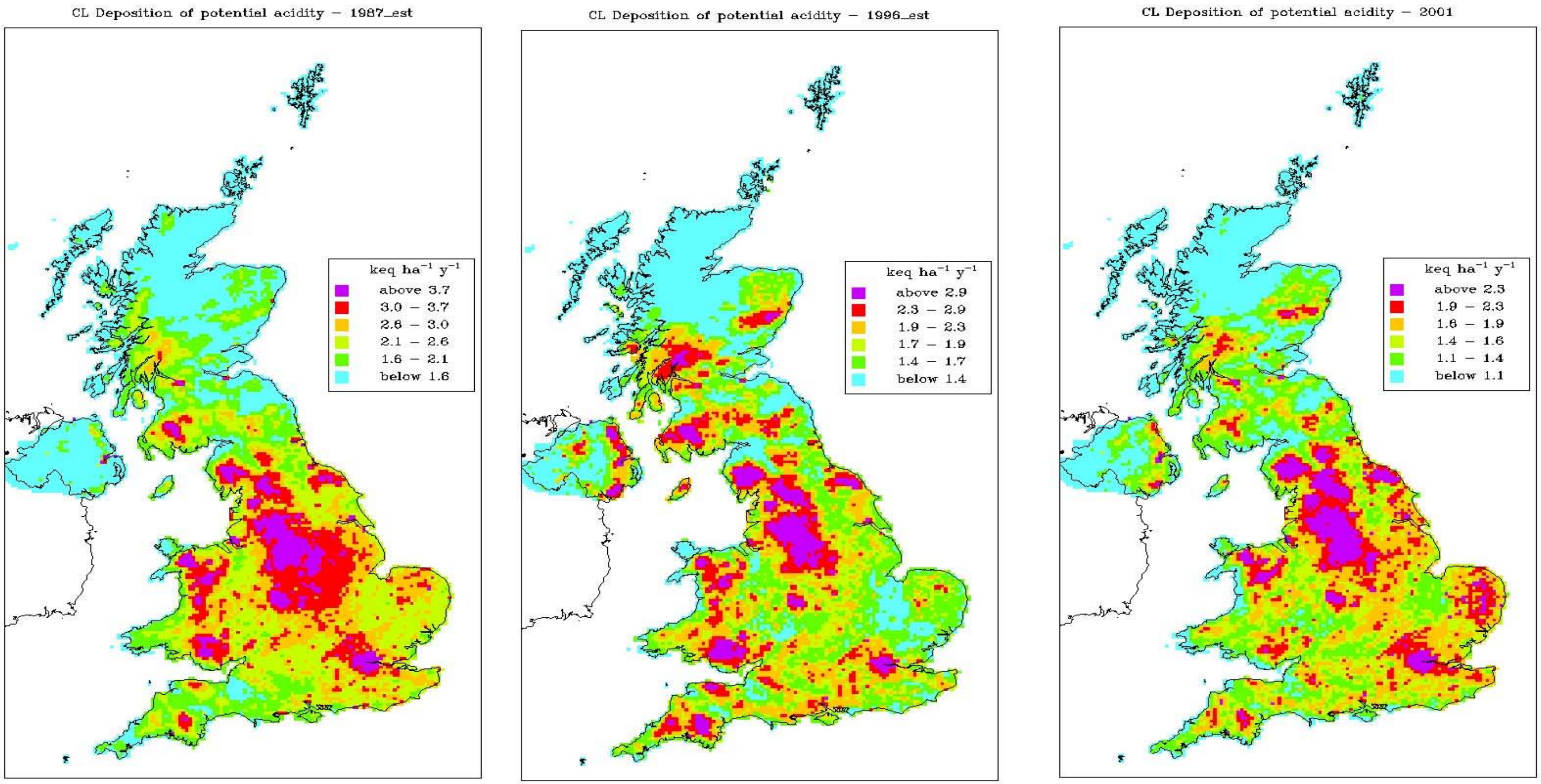


Figure 4.12. Total acidifying inputs 1987 (estimated), 1996 (estimated) and 2001

4.3.6. AEROSOL DRY DEPOSITION

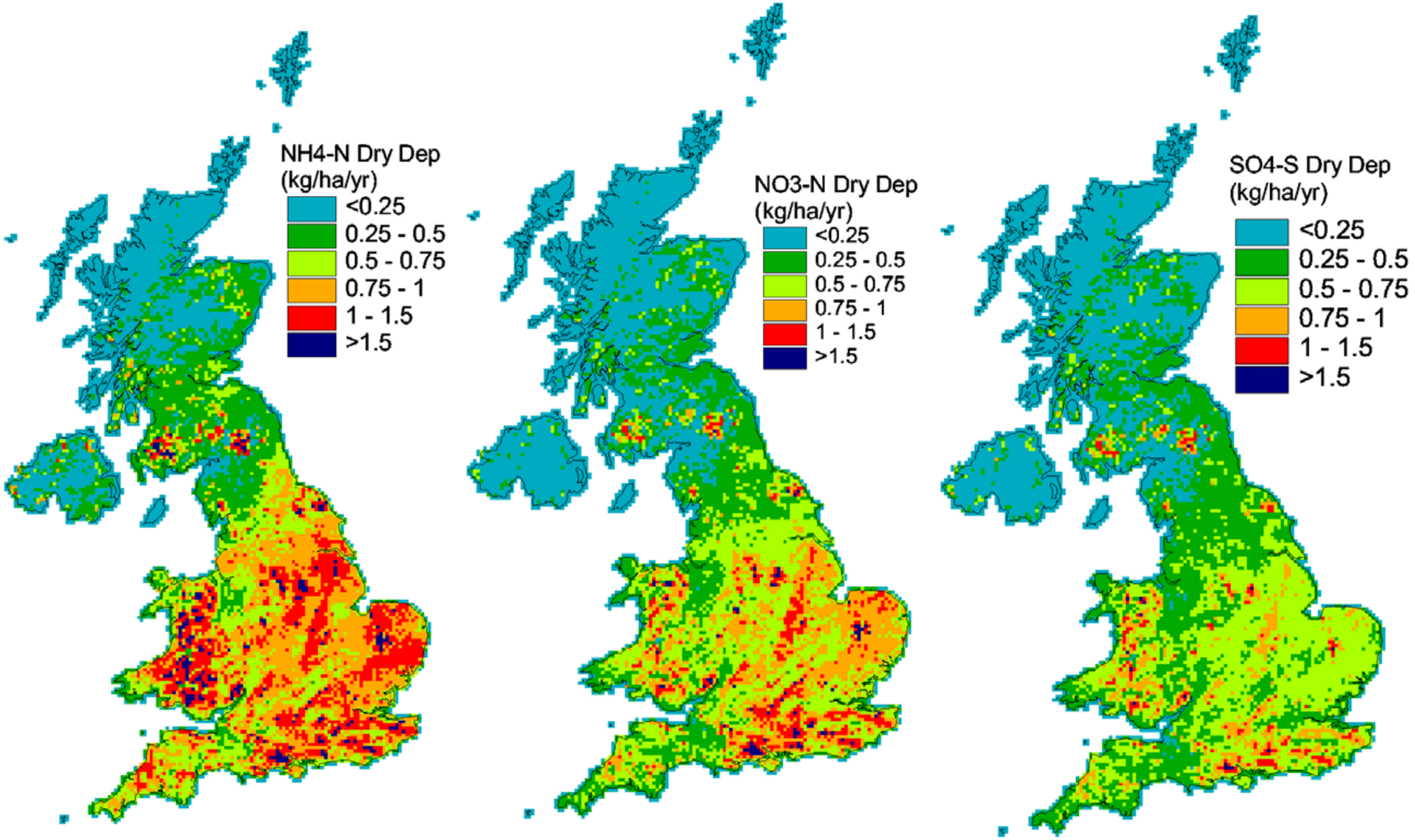


Figure 4.12. Aerosol dry deposition fields of NH_4^+, NO_3^- and SO_4^{2-}, derived from the air concentration field measured with the UK Ammonia and Nitric Acid Monitoring Networks.

A first measurement based estimate of the dry deposition fields of aerosol NH_4^+, NO_3^- and SO_4^{2-}. The Nitric Acid Monitoring Network has been operating since September 1999. For reasons of comparability with the wet deposition maps data, the analysis uses the first two complete years (2000 and 2001) of data from the Nitric Acid Network for NO_3^- and SO_4^{2-} (12 sites) and the equivalent data from the Ammonia Monitoring Network for NH_4^+ (41 sites). Both datasets show clear smooth concentration field with highest concentrations in the SE and lowest concentrations in the NW. There is excellent correlation between sites between the two years with very little inter-year variability. Hence the concentration data of the two years were averaged for the calculation. From these measured concentrations, measurement based concentration fields were derived for the UK by bi-linear interpolation.

Dry deposition velocities (V_d) are based on micrometeorological flux measurements of the dependence of V_d on particle diameter (d_p) and turbulence (u_*) for forest, crops and grassland (Gallagher et al., 1997; Joutsenoja, 1992; Nemitz et al., 2002). The typical size distributions of the aerosol in the UK was derived from four months measurement data using an Aerodyne Aerosol Mass Spectrometer (AMS, Jayne et al., 2000). This instruments measures the size distribution of (semi-)volatile aerosol components in the size range 0.03 to 1 μm. This includes all NH_4NO_3 and $(NH_4)_2SO_4$, but not refractory aerosol constituents like $NaNO_3$, which is typically associated with coarse-mode sea salt. Therefore, in addition to the AMS results, 20% of the NO_3^- were assumed to be contained in the coarse mode. These size distributions were used to calculate bulk values of V_d/u_* for each aerosol species.

A map of average wind speed across the UK was used to calculate u_* values and, from these, values of V_d for each major landcover type in each 5 km grid cell. From these values a land-cover weighted average deposition velocity was calculated and applied to calculate the average deposition in the grid cell.

The resulting maps (Fig. 4.12.) clearly reflect the locations of the major UK forests, representing the fact that V_d to forest exceeds the grassland values by a factor of typically 15. This would imply that aerosol dry deposition, although a minor contributor to the total UK budget of N and S deposition, makes an important contribution to the deposition to forests, an ecosystem type most at risk from N deposition. However, it must be emphasised that values of V_d are derived from very few studies. For example, the measurements for forest used here were made over a very mature forest in the Netherlands and may overestimate the deposition to the ‘average’ UK forest. Therefore, further work in this area should focus on micrometeorological measurements of the aerosol dry deposition velocity to UK vegetation and in particular to forests.

The current estimates of the country totals are 16.7 kt NH_4^+-N, 12.9 kt NO_3^--N and 11.1 kt SO_4^{2-}.

4.3.7. OROGRAPHIC COMPONENT OF WET DEPOSITION

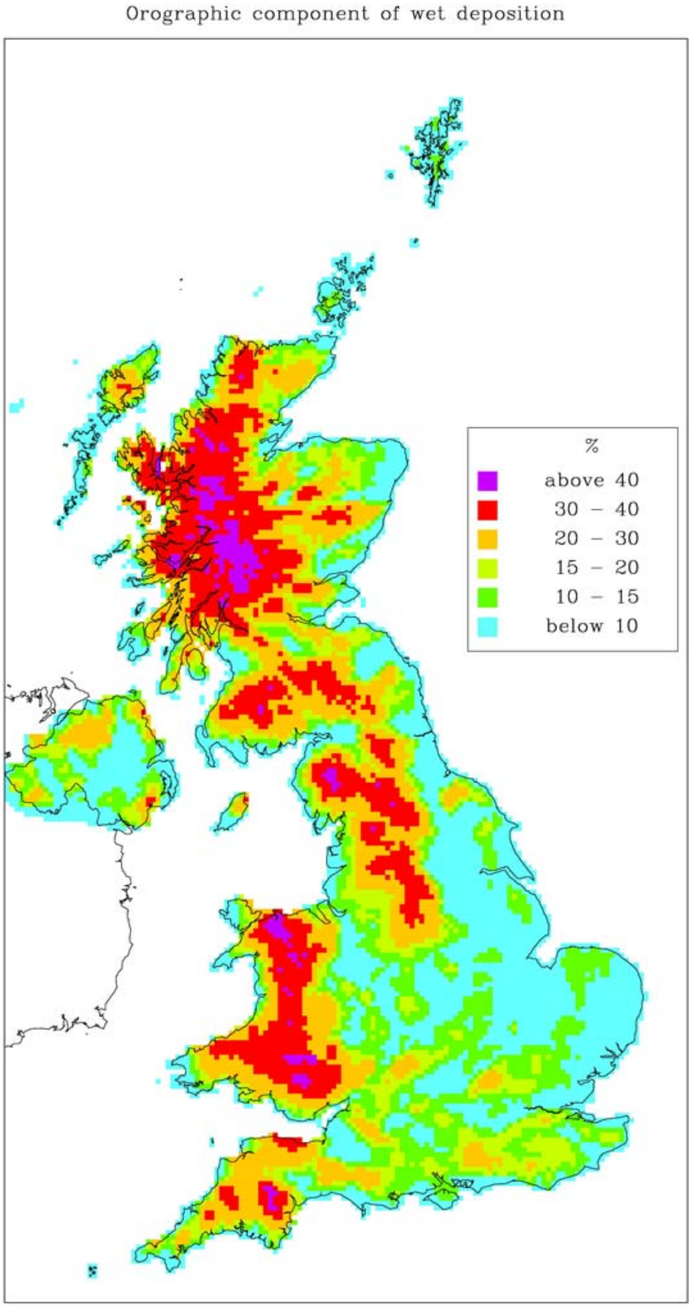


Figure 4.13. Orographic component of wet deposition in theUK

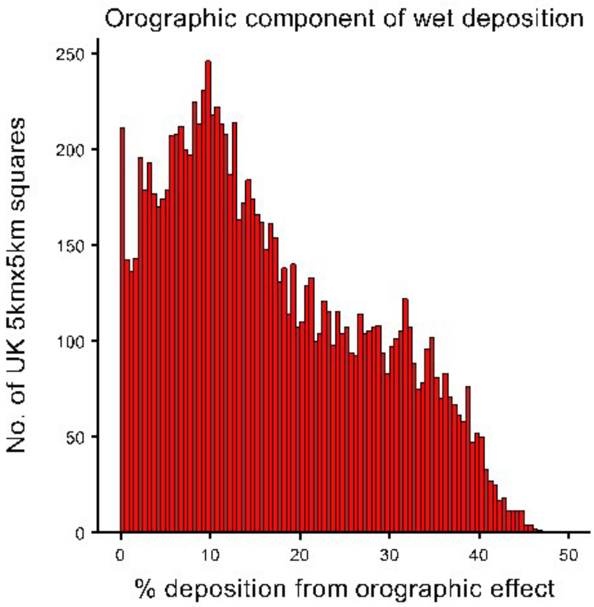


Figure 4.14. Frequency histogram for orographic component of wet deposition

A more detailed justification for the use of an orographic enhancement of wet deposition in the UK is discussed in the Appendix to this report. In summary, the science shows us, through several focussed studies of hill cloud and rainfall, that both the rainfall amount and the ion concentration of pollutants in rainfall increase with altitude. There is no direct relationship with altitude, the effect being primarily driven by frontal rainfall in the UK scavenging both extra rain and extra pollutants as it falls through the cap clouds associated with high hills and mountain ranges.

Studies have show consistently that this effect exists across the whole country, but there is considerable variation in the amount of the enhancement at different times of year, at different locations across the country and for the different pollutant ions. However, the increase in annual average wet deposition from this effect is relatively consistent and the current wet deposition model applies the same methods to estimate the orographic effect across the whole UK. This assumes that rainfall falling through cap cloud has a pollutant concentration (when it hits the ground) which is twice that of rainfall coming directly from frontal systems. Although the model does not explicitly consider convective rainfall (thunderstorms, etc.), if the spatial pattern of convective rainfall is relatively random at the 5km scale there is no bias introduced by applying this procedure everywhere.

The average orographic component of wet deposition for the period 1999-2001 is mapped in Figure 4.13. along with the frequency histogram for the approximately 11000 5km x 5km squares in the UK in Figure 4.14.. The enhancement is greatest in the mountain areas with consistently 30% or more of the wet deposition from orographic enhancement. The average enhancement across the whole country is around 15% but this is combined with the differing patterns of pollutant ion concentration to give different effects on the budget for different ions. For the major components of acidification (oxidised Sulphur, oxidised Nitrogen and reduced Nitrogen), the budget numbers are quite consistent (Table 4.2.).

Table 4.2. Wet deposition from orographic enhancement for oxidised sulphur, oxidised nitrogen and reduced nitrogen

Component	Rain * rain ion concentration	Orographic addition	UK wet deposition	% wet deposition from orographic effect
Oxidised Sulphur	106	28	134	20.9%
Oxidised Nitrogen	77	20	97	20.5%
Reduced Nitrogen	88	22	110	19.5%

Acid Deposition Processes: Measurement of ammonia dry deposition and development of process-based models.

EPG 1/3/166

M.A. Sutton, C. Milford, E. Nemitz, D. Famulari, M.Anderson-Dunn, Y.S. Tang, M. Twig, B. Loubet, M. Riedo and D. Fowler

Centre for Ecology and Hydrology
(Edinburgh Research Station)
Bush Estate, Penicuik,
Midlothian, EH26 0QB, UK.

Ammonia measurements

- The environmental consequences of enhanced atmospheric ammonia are being increasingly recognized and include eutrophication of oligotrophic terrestrial ecosystems, acidification of soils and increased atmospheric aerosol loadings affecting atmospheric visibility, global radiative balance and human health.
- International policy instruments are now being developed that include abatement of ammonia, including within the Convention on Long-Range Transboundary Air Pollution, the EU National Emissions Ceilings Directive and the Directive on Integrated Pollution Prevention and Control.
- Fluxes of ammonia between the land and the atmosphere are recognized as being highly uncertain and provide a key limitation to the scientific assessment necessary to underpin the policy developments.
- The NH_3 part of the Acid Deposition Processes project was initiated to provide a focused study and analysis of the biosphere-atmosphere interactions of ammonia under UK conditions in order to improve the quantification necessary to develop sound policy responses. Grasslands were selected as a target ecosystem as they both emit NH_3 to the atmosphere and may be impacted by NH_3 deposition from the atmosphere.
- A substantial effort has been placed in methods development for NH_3 fluxes. New micrometeorological measurement methods have been developed and applied including low-cost gradient methods, a continuous systems for measuring NH_3 fluxes by Relaxed Eddy Accumulation and initial tests with an eddy-covariance system based on TDL-AS. Near source dispersion modelling has also been developed as a new tool for the measurement of NH_3 fluxes.
- The Acid Deposition Processes project has provided the first comprehensive database of NH_3 exchange with grasslands in the UK. The activity represents the international state-of-the-art in NH_3 biosphere-atmosphere exchange.
- The results from the Acid Deposition Processes project have been used to develop a wide range of models including: I) core bi-directional resistance models, II) dynamic models of NH_3 exchange interaction with grassland management and C & N cycling, III) models of within-canopy fluxes, IV) gas-particle inter-conversion models linked to biosphere atmosphere exchange of NH_3, V) short-range dispersion and deposition models, to estimate local sources and establish landscape level interactions through the quantification of advection fluxes.
- The results of the Acid Deposition Processes project are also being used to develop simplified parametrizations of NH_3 exchange that can be used directly in atmospheric transport models. Collaborative work is ongoing to synthesise the UK measurements with other European measurements and to apply the results into the European Monitoring and Evaluation Programme (EMEP) model of the UNECE Convention on Long-Range Transboundary Air Pollution, which will also include efforts to characterize appropriate landcover / landuse maps at the European level. Linked collaboration has also taken place within the EUROTRAC-2 BIATEX sub-project.
- The UK measurements were put into the context of grassland NH_3 exchange across Europe through the linked EU GRAMINAE project, which established a transect of flux measurement stations across Europe. These have used micrometeorological methods and been supported by a series of integrating measurements allowing fluxes to be interpreted and simulated using newly developed numerical models.

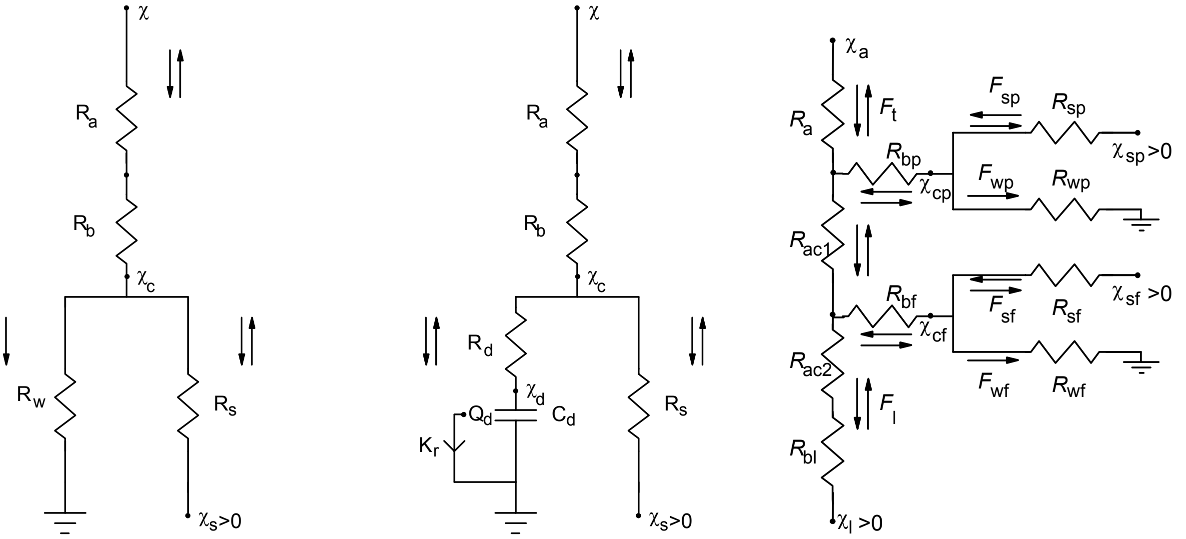
- An integrated experiment on NH_3 exchange was hosted in Braunschweig as a core activity of the GRAMINAE programme. This experiment brought together over 50 scientists in the field to consider the interactions of ammonia exchange from the physiological and within-canopy level, to net fluxes and landscape interactions. A key issue in the experiment was the consideration of flux divergence, either due to advection errors or due to gas - particle inter-conversion.
- Through the collaboration with GRAMINAE, which was a component project of the Terrestrial Ecosystem Research Initiative (TERI) and has taken an active role in seeking productive collaboration between TERI projects, the UK results were synthesized in the frame of the TERI Concerted Action (TERICA).
- The UNECE Convention on Long-Range Transboundary Air Pollution is a key user of the results. GRAMINAE has fed directly into several groups of the Convention, including the Ammonia Expert Group, EMEP and the Task Force on Measurement and Modelling.
- Key inputs from the Acid Deposition Processes project to the Ammonia Expert Group include an analysis of the uncertainties linking NH_3 emissions abatement to atmospheric concentrations and deposition, plus inputs to the revision of the Gothenburg Protocol technical Annex on ammonia abatement methods.
- A priority concern highlighted within the Task Force on Measurement and Modelling is the current inadequacy of European NH_3 and NH_4^+ aerosol monitoring, and recommendations have been made to revise the current monitoring strategy.

5. AMMONIA MEASUREMENTS

5.1. Introduction to ammonia measurements

Ammonia is increasingly recognised as an environmentally important gas, whose deposition leads to the eutrophication and acidification of ecosystems. Following the dramatic reduction of SO_2 emissions from the UK and Europe as a whole, dry deposition of NH_3 is estimated to dominate the deposition of N and potential acidity over wide areas of the UK (NEGTAP, 2001). In addition, atmospheric NH_3 contributes to the formation of NH_4^+ aerosols such as ammonium sulphates and ammonium nitrate, which are highly climate active, contributing to both the direct and indirect aerosol effects. These aerosols also contribute to PM_{10}, which has been associated with human health problems, and to visibility impairment.

In general, ammonia exchange with vegetation is bi-directional; the direction of the flux depends on the comparative magnitudes of the air concentration and the gas concentrations in equilibrium with the ammonium (NH_4^+) concentrations and pH values of the various water pools at the surface. In the simplest case, the only such pool is provided by the leaf apoplast, whose NH_4^+ and pH gives rise to a NH_3 gas concentration in the sub-stomatal cavity, also called the 'stomatal compensation point (χ_s)'. The canopy compensation point resistance model (Fig. 5.1a) describes this pathway through the serial resistances representing transport through the turbulent atmosphere (R_a), the laminar sub-layer that surrounds leaves and other surface elements (R_b) and the stomata (R_s). In addition, this model describes deposition to the leaf surfaces (cuticles) through the cuticular resistance (R_w).



A. **B.** **C.**

Figure 5.1: Diagrams of different 'canopy compensation point' (χ_c) resistance models of NH_3 vegetation-atmosphere exchange available at the start of GRAMINAE. The net flux is described as the result of the exchange between the air concentration (χ) and χ_c, the latter being the result of competition between fluxes with the leaf surface and transfer through stomata (R_s) with a stomatal compensation point (χ_s). R_a and R_b, are the atmospheric resistances to transfer. A key challenge of GRAMINAE has been to revise these models and develop generalized parametrizations relevant for climatic and management differences across Europe.

A, represents a single-layer model (Sutton *et al.* 1995b), with deposition to the leaf surface treated as a simple resistance (R_w).

B, allows a dynamic treatment of cuticular uptake in relation to a cuticular adsorption capacitance (C_d) of charge Q_d. R_d is the adsorption resistance and K_r a reaction rate depleting Q_d (Sutton *et al.* 1998).

C, shows a steady-state three-layer model including emissions from leaf litter according to χ_l and diffusion through the canopy limited by R_{ac} and R_{bl} distinguishing the overlaying canopy into pod (p) and foliage (f) layers (Nemitz *et al.* 2000a).

In a more complex approach, the leaf surfaces provide an additional pool enabling bi-directional transfer. As a leaf water layer dries out, its NH_4^+ concentration increases and it may give rise to an equilibrium NH_3 gas-phase concentrations that exceeds the ambient concentration. Cuticular desorption would result. The capacitance model (Fig. 5.1b) is able to describe this process by dynamically modelling the NH_3 stored on leaf levels by analogy with an electrical capacitor. For certain plant canopies, distinct layers in the canopy may have different values of χ_s (Fig. 5.1c) and soil moisture or decomposing plant litter may provide an additional water pool near the ground, giving rise to a ground-level compensation point (χ_l). While the latter resistance models provide valuable research tools to understand the in-canopy cycling and exchange processes of NH_3, the canopy compensation point model may satisfactorily predict exchange fluxes in most conditions and provides an approach that is sufficiently simple for generalized application in atmospheric transport models, most of which currently can only describe deposition.

This report reports on recent progress in the study and understanding of NH_3 exchange within the Acid Deposition Processes. In this work

(I) fluxes were quantified directly by measurement, including the development of new measurement techniques,
(II) process based models for understanding ammonia exchange process interactions have been developed, and
(III) the basis has been provided to describe ammonia exchange in up-scaling to the UK in (a) CEH deposition model (Part 4, applied for NEGTAP), in (b) the FRAME model (Part 6) and in (c) the EMEP model (contribution in kind to EMEP project).

Significant added value to the project was provided through the lead role CEH played in the EU project GRAMINAE 'GRassland AMmonia INteractions Across Europe' and in the EUROTRAC-2 subproject BIATEX-2 (BIosphere / ATmosphere EXchange). This international collaboration provided the basis to analyse the UK NH_3 flux measurements in the context of a European transect across climate and farm management regimes. CEH development of measurement techniques were co-ordinated with complimentary initiatives at other European institutes and landscape modelling approaches, developed elsewhere, were extended to the UK.

This chapter provides an overview over recent method and instrument development for NH_3 flux measurements at CEH and their performance in the UK and during an international intercomparison campaign. It presents the results of long-term NH_3 flux measurements at three UK field sites (Easter Bush, Auchencorth Moss and Plynlimon) using novel low-cost technology and detailed measurements at Easter Bush with a state-of-the-art analyser, which are analysed to provide high temporal resolution measurement, study the effects of management and provide seasonal information and annual budgets. The data are analysed in the context of measurements along a European transect.

The chapter further reports on new detailed process level model development and its application to the Easter Bush field site. New parameterisations of NH_3 exchange have been derived from new and existing measurements and their generalization for the application in national and regional atmospheric transport models. Finally, the chapter describes how new developments and parameterisations are being used to underpin policy development at the national and European level.

5.2. Development and application of methods to measure ammonia dry deposition

5.2.1. METHODS APPLIED

Conventionally fluxes of ammonia are derived by the aerodynamic gradient method, from the measurement of vertical concentration gradients and information on atmospheric turbulence, provided by an ultrasonic anemometer. In the past concentrations were measured manually, with filter packs or dry batch denuders, averaging over typically 1 to 3 hours. The AMANDA gradient system (ECN, Petten, NL), enables concentrations to be measured continuously at three heights, using rotating wet denuder inlets with online analysis using a selective ion membrane and conductivity cell, providing gradients every 7.5 minutes. Several AMANDA systems have been operational at CEH Edinburgh for ten years and the operational procedures have been refined so that long-term measurements can now be made with good data capture. Two drawbacks of this state-of-the-art method have prompted the development of alternative techniques at CEH Edinburgh:

1. The gradient technique derives a flux that is averaged over the height-range of the measurements. Micrometeorological flux measurements are made within the layer where fluxes are height-independent. However, NH_3 forms equilibriums with HNO_3 and HCl and reacts with H_2SO_4. These important reactions lead to sources and sinks of NH_3 in the atmosphere and can result in fluxes that change with height (e.g. Nemitz *et al.*, 2004a). In addition, local (agricultural) point sources can lead to advection errors and often complicate the interpretation of the measurements (e.g. Loubet *et al.*, 2002). Both effects can only be quantified reliably if fluxes can be measured at several individual heights. Single-height flux measurements are also required in logistically challenging situations, such as above forest, urban areas or from aircraft platforms. Two alternative concepts derive fluxes from measurements at a single height: eddy covariance requires fast response concentration measurements (several Hz), while relaxed eddy accumulation requires fast switching of the air sample, followed by slow analysis. The implementation of these techniques is complicated by the stickiness of ammonia.
2. AMANDA is expensive in terms of initial purchase, personnel and power consumption. It can only be applied on a campaign basis or at selected, well-equipped sites with mains electricity and in easy reach of scientific personnel. A low-cost alternative is required, which can be operated at remote sites, to provide long-term integrated dry deposition budgets at a larger number of sites for model validation.

5.2.2. APPLICATION OF AMANDA TO CONTINUOUS FLUX GRADIENT MEASUREMENT

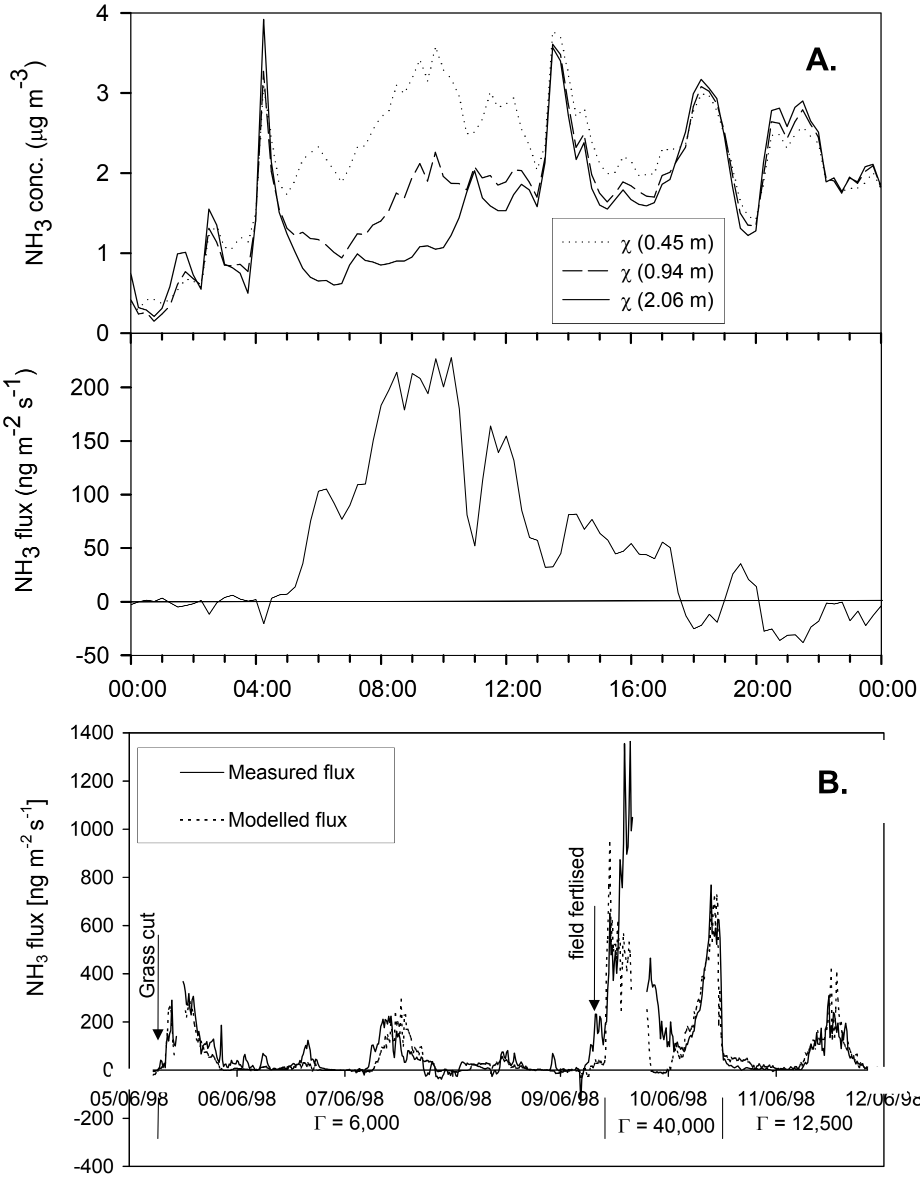
During former Acid Deposition Processes projects, the AMANDA system was initially used to measure long-term concentrations (at a single height) and later for campaign based measurements. More recently, this system has been used for long-term measurements at the CEH Easter Bush grassland site to derive both the fine structure and the seasonal patterns of the exchange (Fig. 5.2). These data provide, for the first time, accurate information on annual totals and the response of the exchange to agricultural management (cut, fertilization, grazing).

DEVELOPMENT OF RELAXED EDDY ACCUMULATION (REA) TO MEASURE AMMONIA FLUXES

Conventionally, with the aerodynamic gradient approach, a single NH_3 exchange flux is calculated from concentration measurements of NH_3 at several heights, together with standard micrometeorological parameters. The gradient technique therefore cannot quantify flux changes with height, e.g. due to effects of advection and chemical conversions. Flux measurements at several individual heights are required to allow flux divergence to be quantified. The two approaches available are the eddy-covariance technique (EC) and the relaxed eddy accumulation technique (REA), e.g. Businger and Oncley (1990). With the latter, the flux (F_χ) is calculated from the difference between the concentrations, during up- and down-drafts ($\chi^+ - \chi^-$) which are conditionally sampled into a two-channel analyser using fast switching valves, depending on the sign of the vertical wind component (w):

$$F_\chi = \beta \sigma_w (\chi^+ - \chi^-) \quad (1)$$

Here σ_w is the standard deviation of *w* and β is a factor of proportionality. A first REA system for NH_3 had been presented by Zhu *et al.* (2000), but this was limited to measurements of daytime fluxes at a time resolution of 2 hrs with manual change over of the bulk dry denuders deployed. A system was therefore developed, in collaboration with UMIST, Manchester, for the continuous automated measurement of NH_3 fluxes using a sensitive state-of-the-art online analyser (Figure 5.3).



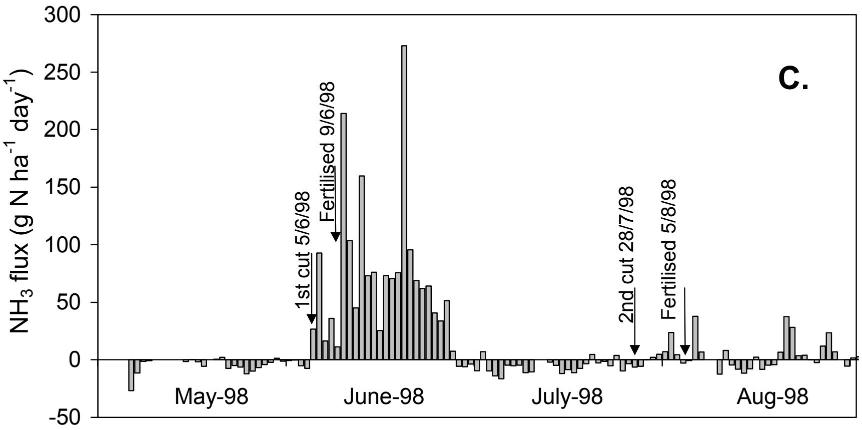


Figure 5.2: Diagram showing long term NH_3 exchange at Easter Bush on different timescales: A) diurnal, B) weekly and C) seasonal.

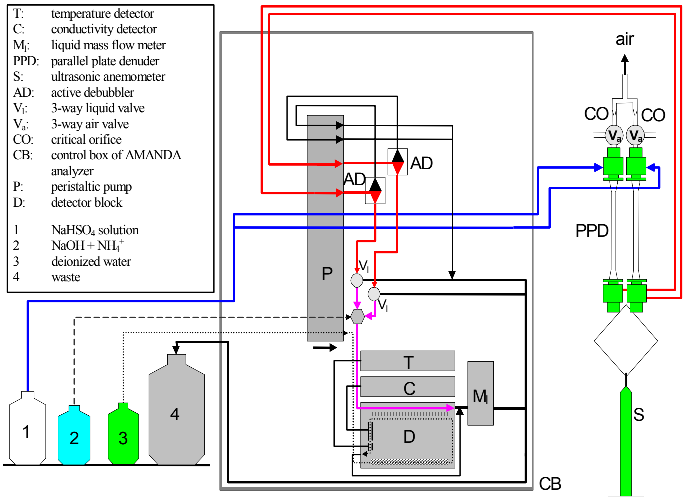


Figure 5.3. Schematic of the continuous relaxed eddy accumulation system (Nemitz *et al.*, 2001a).

This work included the development of the inlet and sampling systems, analysers and the software for switching and control. The REA system uses high flow wet effluent denuder inlets and a diffusion membrane / conductivity analyser for NH_4^+. A referencing mode was incorporated into the system, during which the inlet valves are sampled arbitrarily, to quantify and correct for systematic differences between the channels. Various ways of calculating β (e.g. from the sensible heat flux), $\overline{w}$ and incorporating deadbands were explored.

The system was tested at the Easter Bush field site (Figure 5.4) prior to an inter-comparison with gradient analysers and three other REA systems as part of the GRAMINAE Integrated Experiment at Braunschweig. Given a certain flux, the concentration difference between the up- and down-draft that needs to be resolved for REA is much smaller than the concentration difference between the different heights for the gradient method, pushing the accuracy of current wet chemistry systems, especially in windy conditions, when σ_w is large. Although much progress has been made in lowering the flux detection limit to about 50-100 ng m^{-2} s^{-1}, the accuracy of ca. 25 % is still insufficient to resolve a typical flux divergence of 10 % that might occur due to gas-to-particle conversion or advection. Hence flux divergence for NH_3 could only be measured at present for the most extreme cases of advection adjacent to strong NH_3 sources.

Nevertheless, the Acid Deposition Processes project and GRAMINAE have made available operational REA systems for flux measurements for single-height flux measurements in logistically difficult situations. For example, a prototype REA system based on the same switching system, but using 2-hour filter packs for collection media, was also deployed 65 m above Edinburgh city centre to provide the first direct measurements of urban NH_3 emissions (Nemitz *et al.*, 2001). These initial measurements suggested average emissions strengths of 40 ng m^{-2} s^{-1} (equivalent to 12 kg ha^{-1} yr^{-1}), twice as much as estimated by current emission inventories.

5.2.4. Initial testing of Tunable Diode Laser Absorption Spectroscopy (TDLAS) to measure ammonia fluxes by Eddy Correlation.

For NH_3, implementations of eddy-covariance techniques has long been hampered by the need for analysers that are sufficiently fast (several Hz) and sensitive (< 1 ppb) to measure NH_3 fluxes at ambient conditions. Shaw *et al.* (1998) first demonstrated the feasibility of NH_3 eddy covariance measurements using a tandem mass spectrometer. Recent developments of fast-response sensors for NH_3 include tunable diode laser absorption spectrometers (TDL-AS, based on either lead-salt or quantum cascade lasers) and chemical ionisation mass spectrometers (CIMS) (Zahniser *et al.*, 1996; Nowak *et al.*, 2002).

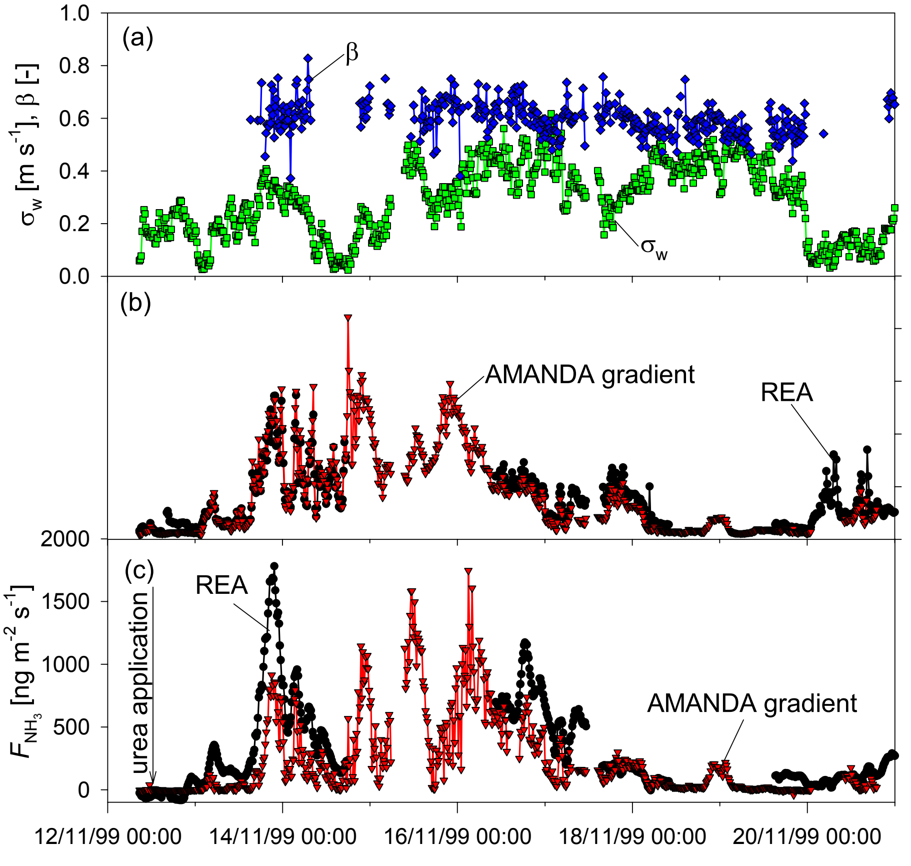


Figure 5.4. Example time series of intercomparison of CEH/UMIST REA system with AMANDA gradient system after urea application at the Scottish Easter Bush site. Shown are the REA coefficient (β), the standard deviation of the vertical wind component (σ_w) as well as the concentrations (χ_{NH_3}) and fluxes (F_{NH_3}) measured with the two systems.

An eddy-covariance system for NH_3 based on a two-channel lead-salt TDL (Figure 5.5) is currently developed as part of two studenships at CEH and provides added value to the instrument development part of the Acid Deposition Processes project. Figure 5.6 shows preliminary example data of a two-day measurement period at Easter Bush.

Figure 5.5. Dual-channel NH_3/HNO_3 lead salt tunable diode laser tested for eddy-covariance measurements at Easter Bush.

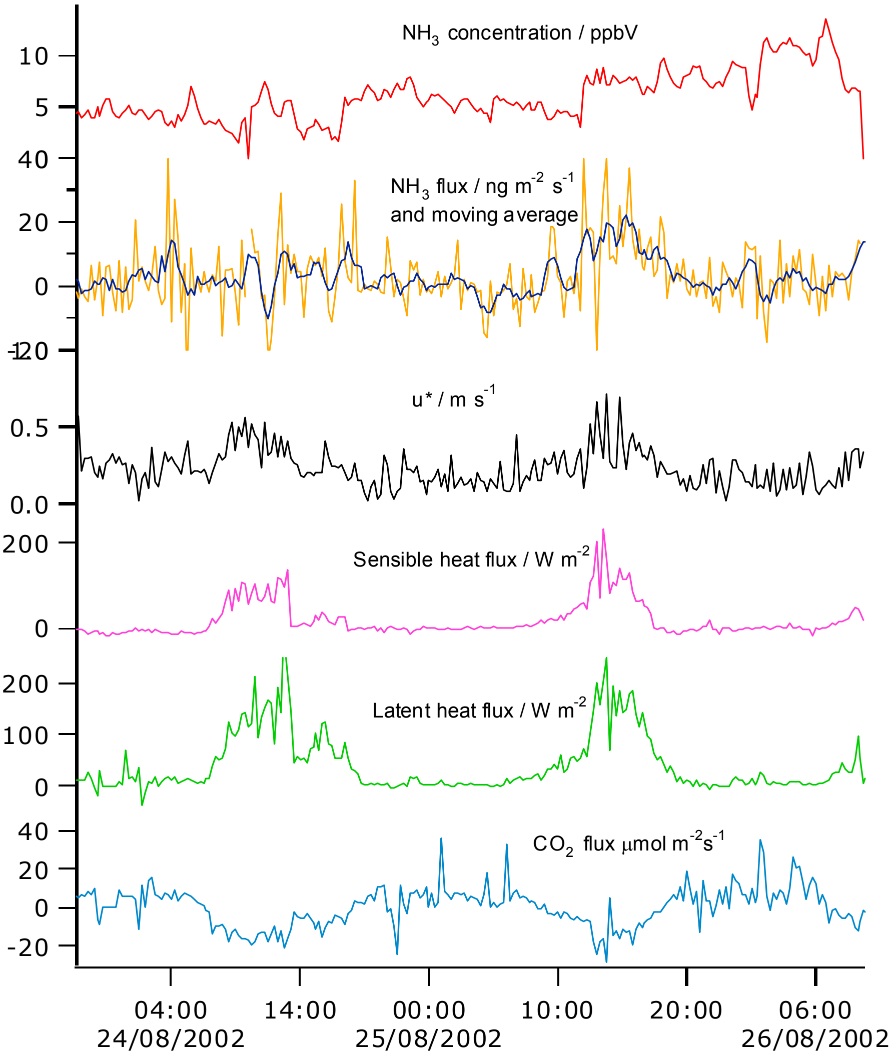


Figure 5.6. Values of NH_3 concentration, flux, friction velocity, sensible heat flux, latent heat flux, CO_2 flux (from top to bottom). Shown values were recorded on Easter Bush field site from 24th August at midnight, until 26th of August at 9 in the morning.

5.2.5. DEVELOPMENT OF THE TIME AVERAGE GRADIENT (TAG) METHOD TO MEASURE LONG-TERM AMMONIA FLUXES.

The second instrument development objective was the construction of a low-cost system for long-term monitoring of NH_3 dry deposition. In the Time Averaged Gradient (TAG) method, developed by CEH, vertical concentration gradients are measured over periods of typically two weeks, using denuder tubes similar to those deployed in CEH's delta samplers (Sutton et al., 2003). In the standard aerodynamic gradient method (AGM), concentration gradients are averaged over typically 1-3 hours and fluxes are calculated using information on turbulence (friction velocity, u_*) and atmospheric stability (Monin-Obukhov stability parameter, L), averaged over the same period. In principle, there is therefore confounding between changes in atmospheric stability and vertical gradients in concentration, so that it is not possible to apply long-term sampling (e.g. fortnightly) to the aerodynamic gradient method. The TAG approach deals with this by applying conditional sampling depending on atmospheric stability. In the simplest approach, relevant to windy Scottish conditions, a single gradient can be applied which is turned off in low-wind conditions, which are associated with very large gradients that would bias the long-term gradient. By contrast, in warmer climates, such as Greece, further stability classes are needed to deal with the wide range of conditions. In this case, the two stability-class system was replaced with a four-class system (stable, neutral, unstable, off). Figure 5.7 shows a 3-height TAG system at the Plynlimon upland site, powered by a combination of wind and solar power.

Figure 5.7. Time Averaged Gradient (TAG) stystem for NH_3 at Plynlimon (right mast), powered by wind and solar power (left mast).

A CEH TAG system was operated at a remote field site of the Greek GRAMINAE project partner, where it was compared with a passive flux sampler (PFS). The PFS suffered from sampling problems of low wind-speeds. By contrast to the PFS the TAG system was found to be more robust in sampling concentrations, as this uses active air sampling to denuders at a constant 0.3 l min^{-1}. While the often PFS system overestimated concentrations, comparison of the PFS and TAG system at the Greek site showed that it was able to obtain agreement between the two methods in relation to fluxes for some periods (Figure 5.8). For other periods the agreement was less encouraging, and this remains a topic for further investigation e.g. in relation to micrometeorological and implementation constraints.

5.2.6. ESTIMATING AMMONIA FLUXES WITH A NEAR-SOURCE PLUME DISPERSION MODEL

Most methods for estimating NH_3 fluxes rely on the determination of concentration changes within the immediate turbulent boundary layer of the canopy, either by the vertical profile (gradient methods), instantaneous fluctuations in concentration (eddy correlation) or average differences between up- and down-draughts of air (eddy accumulation). As part of the GRAMINAE Integrated Experiment, however, a new method was developed in collaboration with the French team, which simply compares the average concentration above the canopy with the atmospheric background concentration (Loubet *et al.* 2004). As the differences in concentration are much larger than the surface gradients or fluctuations this potentially provides a much more robust measurement method. By contrast, a constraint is the need for a tower to determine background NH_3 concentrations in parallel, and this was provided during the Integrated Experiment by measurements at 43 m on a tower of the Physikalisch-Technische Bundesanstalt, around 2 km W of the field site.

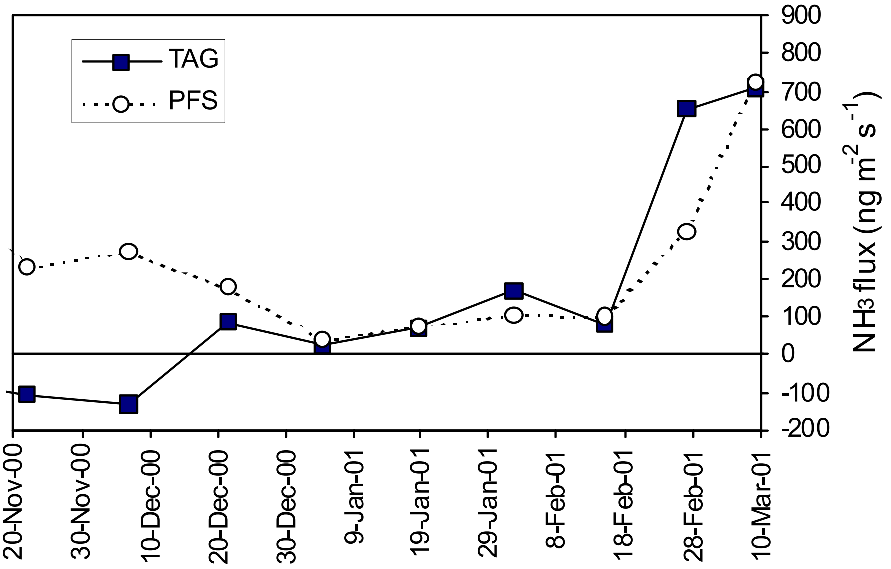


Figure 5.8. Comparison of two low-cost ammonia flux measurement systems at the Greek GRAMINAE site. The conditional time-averaged gradient (TAG) system is compared against the passive flux sampling (PFS) system.

The principle of the method is to apply a near-source dispersion model (Loubet *et al.* 2001), which relates the concentration enhancement above background and the meteorological exchange parameters to the NH_3 flux. The model referred to as FIDES (Flux Interpretation by Deposition and Exchange over Short-range) was initially developed to address advection issues in flux measurements, but can equally be applied to estimate surface fluxes. In order to apply this method, a large uniform field is required so that concentrations above the field are controlled primarily by the field itself.

5.3. Results of flux measurements

5.3.1. CONTINUOUS AMMONIA FLUX MEASUREMENTS AT EASTER BUSH AND THE EFFECT OF LAND MANAGEMENT.

Figure 5.9 shows NH_3 concentrations at three heights above the grass canopy at the Easter Bush intensive grassland site for two contrasting days; 27 May and 7 June 1998 (Milford *et al.* 2001b, Sutton *et al.* 2001a). The fine detail of the measurements is demonstrated, with switches from net deposition to emission being evident on 27 May at 08:00 and on 7 June at 04:30 and 17:30. The high-resolution NH_3 data along with detailed accompanying meteorological data enable the mechanisms and controls on NH_3 exchange to be investigated. In particular, these measurements at the Scottish site illustrate the strong influence of management activities on the net NH_3 exchange: the grass was cut for silage on 5 June 1998 and immediately following the cutting the grassland starting emitting NH_3, up to 380 ng m^{-2} s^{-1}, (Figure 5.10). These emissions are an order of magnitude greater than the typical emission observed over the grassland before cutting. These are the first UK measurements to investigate these interactions of NH_3 fluxes with grassland management.

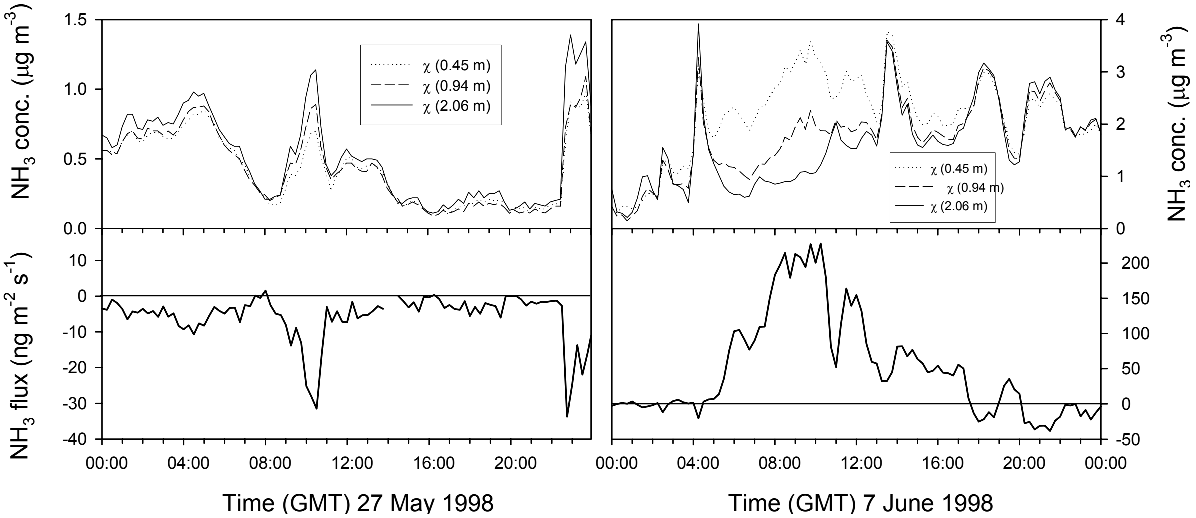


Figure 5.9. NH_3 concentrations at three heights and calculated flux at Easter Bush, Scotland for a) 27 May 1998, a typical day before grass cutting and b) 7 June 1998, 2 days after the cut.

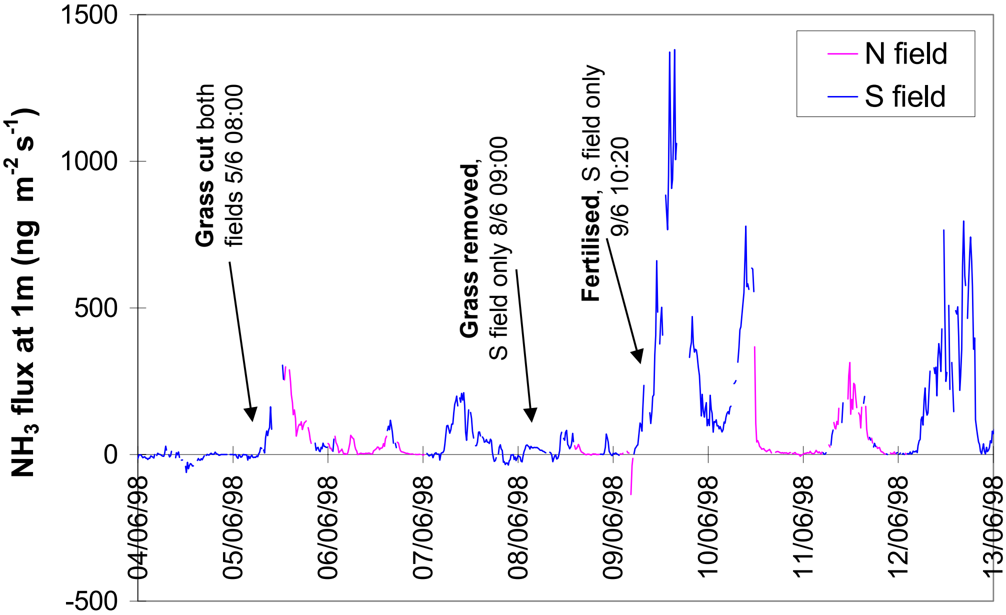


Figure 5.10. NH_3 flux at the Scottish site, 4-13 June 1998, arrows show timing of management activities. Fluxes arising from the North and South field are separated, as the timing of management activities was different for the 2 fields (Milford *et al.* 2001b).

Figure 5.11 provides an overview of the seasonal evolution of daily averaged fluxes observed during the 18 month measurement period at Easter Bush. During the growing season (January – June, period 1) and the dormant winter period 4, small deposition fluxes are generally observed. Grass cutting at the beginning of June and end of July leads to emissions (period 2), which are further enhanced, as expected, after fertiliser application (to 1400 ng m^{-2} s^{-1}), period 3. The combination of larger emissions from cutting and fertilisation lasts for ~3 weeks. During the grazing period (August to January, period 5), the grassland acts as an overall source of NH_3, originating from livestock excretion.

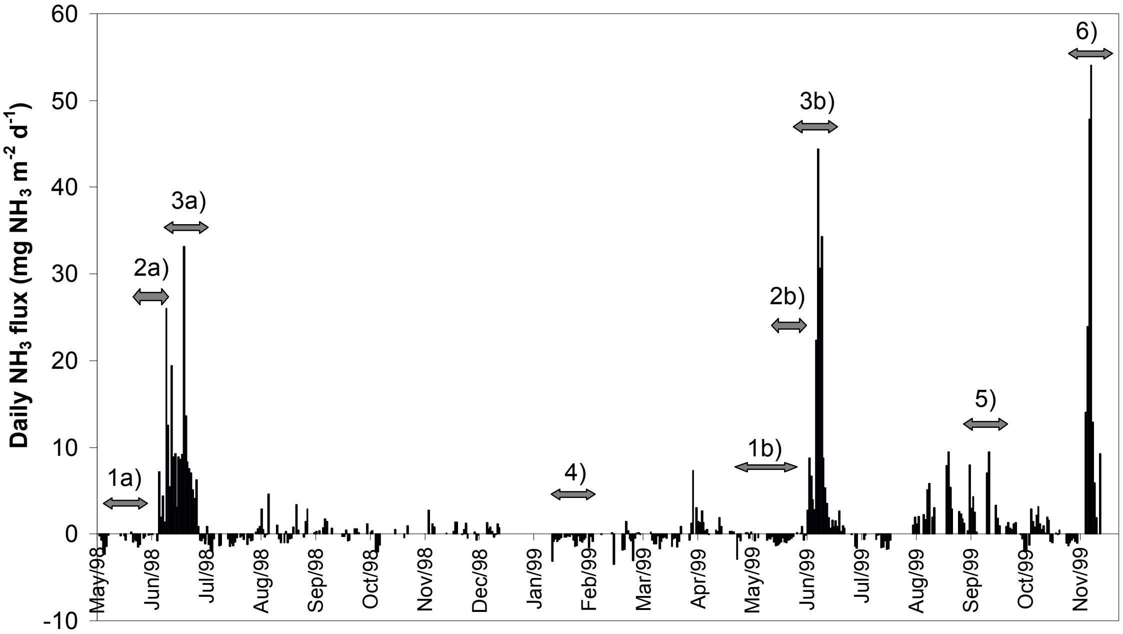


Figure 5.11. Daily fluxes of NH_3 at Easter Bush (only presenting daily fluxes where data capture > 65%). Arrows indicate key periods of NH_3 exchange: 1) Pre-cut, 2) Post-cut, 3) Post-fertilisation, 4) Winter, 5) Grazing and 6) Urea application, a and b indicate periods in 1998 and 1999, respectively.

Figure 5.12 shows the accumulated NH_3–N flux for Easter Bush in 1998 and 1999 and indicates the large contribution to the overall emission from the first cut and fertilisation. It also demonstrates that the pattern of exchange is similar between the 2 years although the grazing emissions are larger in 1999 (Milford *et al.* 2001b).

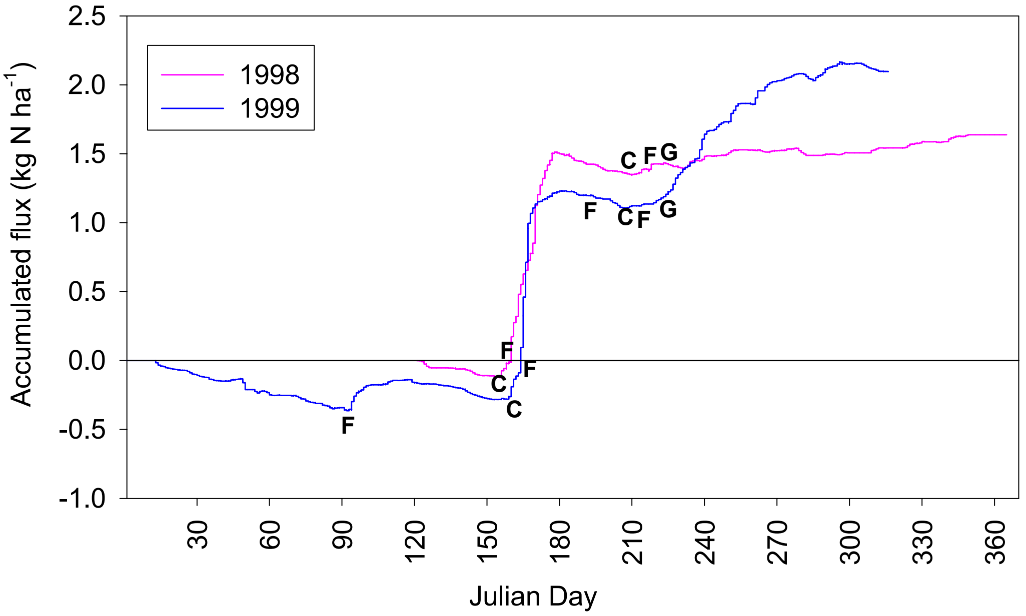


Figure 5.12. Accumulated NH_3-N over the 2 field seasons at Easter Bush, Scotland. 'C' indicates cutting, 'F': $NH_4^+NO_3^-$ fertilisation and 'G': grazing. Timing of cutting was julian day 156 and 209 for 1998 and 153 and 209 for 1999. Timing of fertilisation was julian day 160 and 217 for 1998 and 94, 162, 199 and 214 in 1999. Grazing started on julian day 222 in both years.

5.3.2. PLANT AND SOIL MEASUREMENTS TO HELP INTERPRET AMMONIA EXCHANGE

The measurements presented above show how NH_3 fluxes vary rapidly on diurnal, weekly and seasonal timescales. Diurnal changes in NH_3 fluxes are known to depend on short-term variations in temperature, windspeed, atmospheric stability and canopy wetness (Erisman and Wyers 1993, Sutton *et al.* 1995a), whilst longer scale changes in NH_3 fluxes depend on soil and foliar N supply, and in particular the value of the NH_3 stomatal compensation point (Schjoerring *et al.* 1998, Sutton *et al.* 1998). In order to interpret the NH_3 fluxes in relation to these environmental and biological conditions, detailed accompanying measurements were made of a suite of micrometeorological, vegetation and soil parameters. The measurement protocol was developed after consultation with experimental scientists, as well as modellers in the EU projects GRAMINAE, MEGARICH and MAGEC.

The environmental drivers at Easter Bush and their links to NH_3 fluxes are shown in Figure 5.13. It is of particular interest to note the measurements of canopy wetness, which were made by directly recording the electrical conductivity of leaf surfaces using the methodology of Klemm *et. al.* (2002). The GRAMINAE project provided the first occasion of canopy wetness measurements conducted alongside measurements of NH_3 exchange. Previous to this, measurements of relative humidity in the air or at the leaf surface have been used to infer leaf wetness, but as is seen in Figure 5.13 and further detailed in Klemm *et al.* (2002), canopy wetness is not always directly correlated with relative humidity.

The influence of wetness, humidity and temperature can be seen on the NH_3 flux: small periods of emission occur at times when the canopy is drying out following periods of wetness, e.g. on the 20th, 22nd and 24th May. This may be due to volatilisation of previously deposited NH_3 on the leaf cuticle. Such a phenomenon has been observed in previous measurements and a dynamic model describing this behaviour was developed by (e.g. Sutton *et al.*, 1998), which was subsequently improved to consider interactions between different pollutants by treating the full chemistry taking place on leaf surfaces (Flechard *et al.*, 1999).

An example of longer-term dynamics in NH_3 exchange is shown in Figure 5.14 alongside measurements of apoplastic NH_4^+, total foliar NH_4^+ and soil NH_4^+ and NO_3^-. These results show an increase in the foliar and soil N after cutting and fertilising, explaining the increases in NH_3 emissions. However, some unexpected observations remain. It may be noted that NH_3 emissions were larger after the first cut than the second cut, but that apoplastic [NH_4^+] and total foliar [NH_4^+] were larger after the second cut. Work to explain this through the development of the PASIM model, was not able to show this large difference in emissions. In the field, however, it appears that there was much more nitrification after the second cut (see high soil [NO_3^-] and low soil [NH_4^+]), which was not simulated by the model. Hence with the plants taking up less N in the form of NH_4^+ the compensation point would be expected to be smaller. It still remains to explain the differences in bioassays, however, this could be due simply to the few samples after the first cut giving high uncertainties (Loubet *et al.* 2002a). It is notable that after the second cut, total foliar [NH_4^+] increases before apoplastic [NH_4^+]. It may be that this increase in total [NH_4^+] is more strongly induced by cutting (which would remobilize existing N in the symplast), whereas apoplastic [NH_4^+] responds more directly to fertilization (which leads to uptake through the xylem to the apoplast).

These integrating measurements serve to help interpret the measured fluxes. However, by also including a comprehensive set of one-off measurements of slowly varying parameters as well as management events in detail the dataset serves to provide the initialization conditions for the PASIM model. The model then allows a functional comparison with the measured fluxes and time course of the various integrating measurements such as biomass, LAI, soil and plant N concentrations and water content.

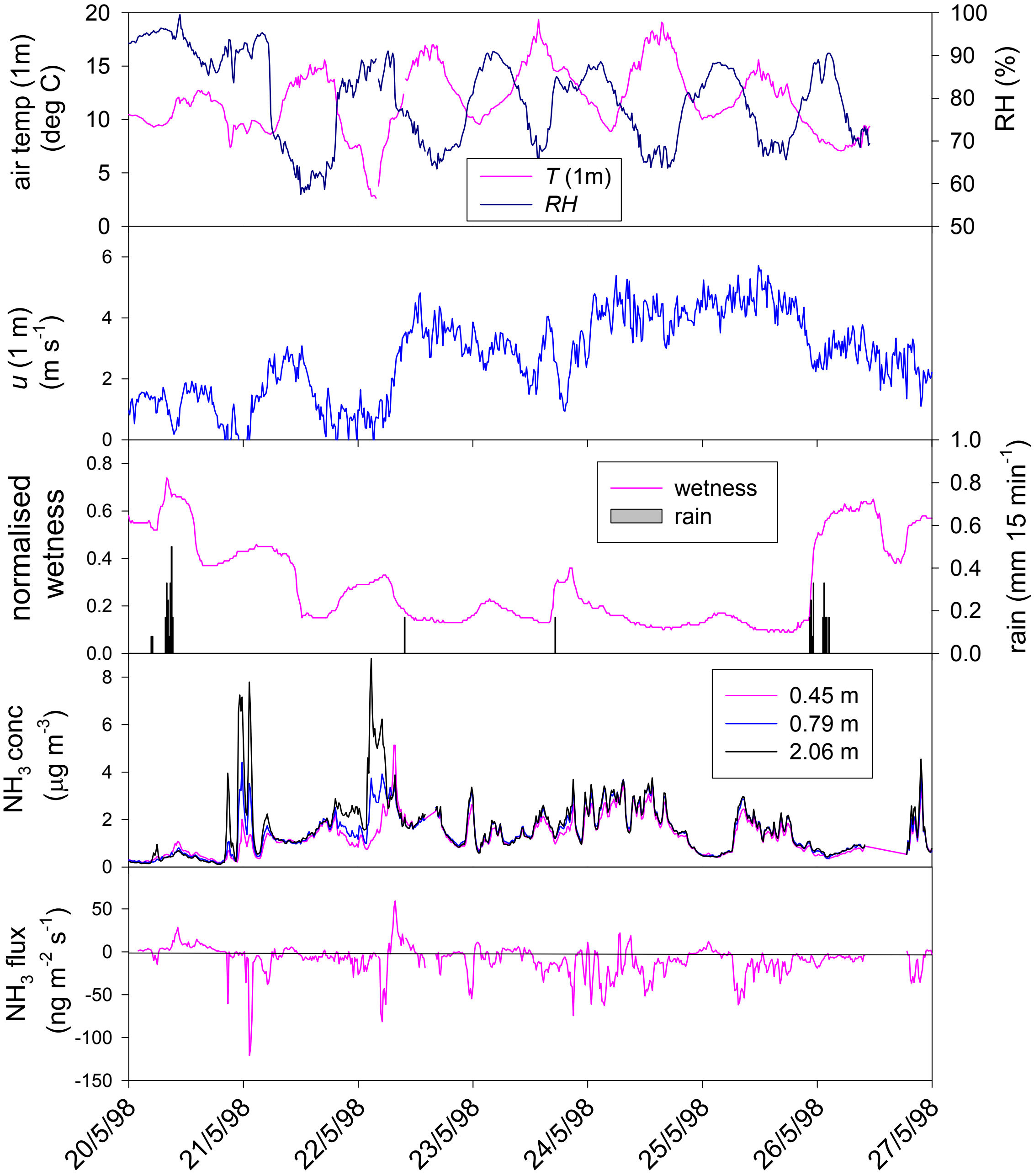


Figure 5.13. NH_3 flux and concentrations at Easter Bush, Scotland, shown alongside measured values of air temp, relative humidity, windspeed, canopy wetness and rainfall. The deposition fluxes with little emission reflect measurements before cutting. Emission peaks may be related to cuticular desorption of NH_3.

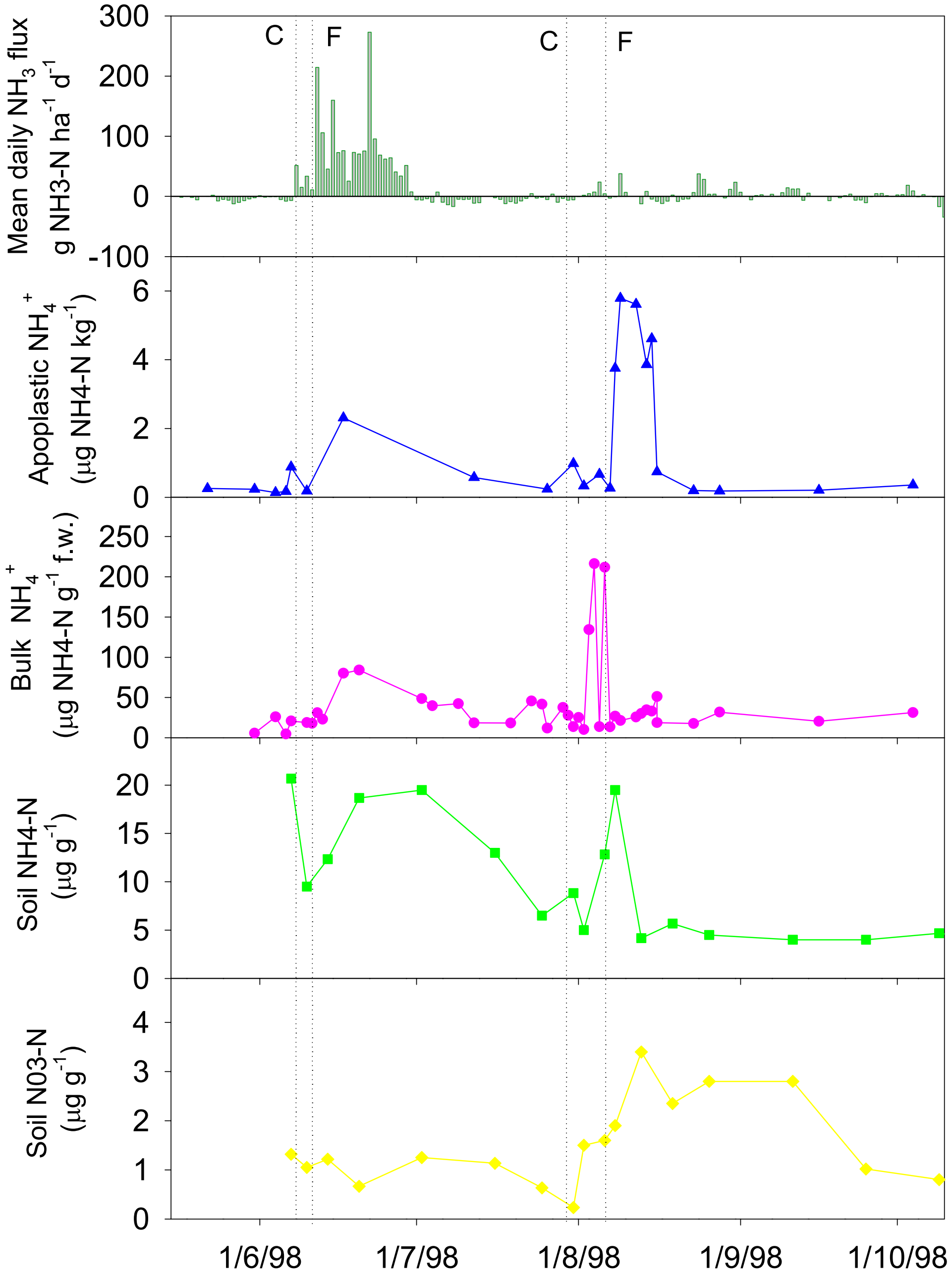


Figure 5.14. Mean daily fluxes at Easter Bush shown alongside measured values of apoplastic and total foliar NH_4^+ and available soil NH_4^+ and NO_3^-. Timing of cutting and fertilisation are indicated by vertical lines.

5.3.3. APPLICATION OF THE TAG APPROACH TO DERIVE LONG TERM AMMONIA DRY DEPOSITION ESTIMATES.

Long-term measurements were made for a year at the Scottish Auchencorth Moss moorland site and for 19 months at the upland site at Plynlimon, Wales, using 3-point TAG systems. The concentrations, fluxes and deposition velocities are shown in Figures 5.15 and 5.16. With the exception of one single period at the end of May 2003, Auchencorth Moss provided a sink for NH_3 at a deposition rate of around 10 mm s^{-1}, which increased into the autumn of 2003 (Figure 5.15).

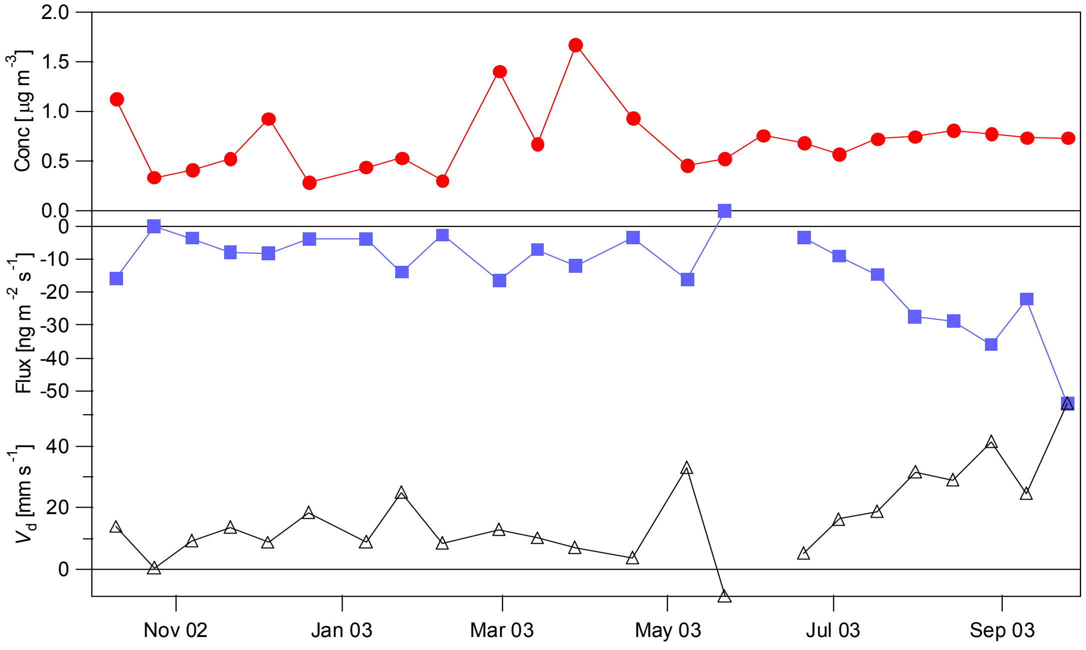


Figure 5.15: Auchencorth TAG results.

By contrast, the exchange at Plynlimon was bi-directional, with emission observed during September 2002 (the warmest and driest month of the year 2002) and throughout the warm summer of 2003. During winter deposition velocities were typically of the order of 20 mm s^{-1} and therefore somewhat larger than at Auchencorth. This is probably due to higher wind speeds at the Welsh upland site facilitating the turbulent transport of atmospheric NH_3 to the vegetation.

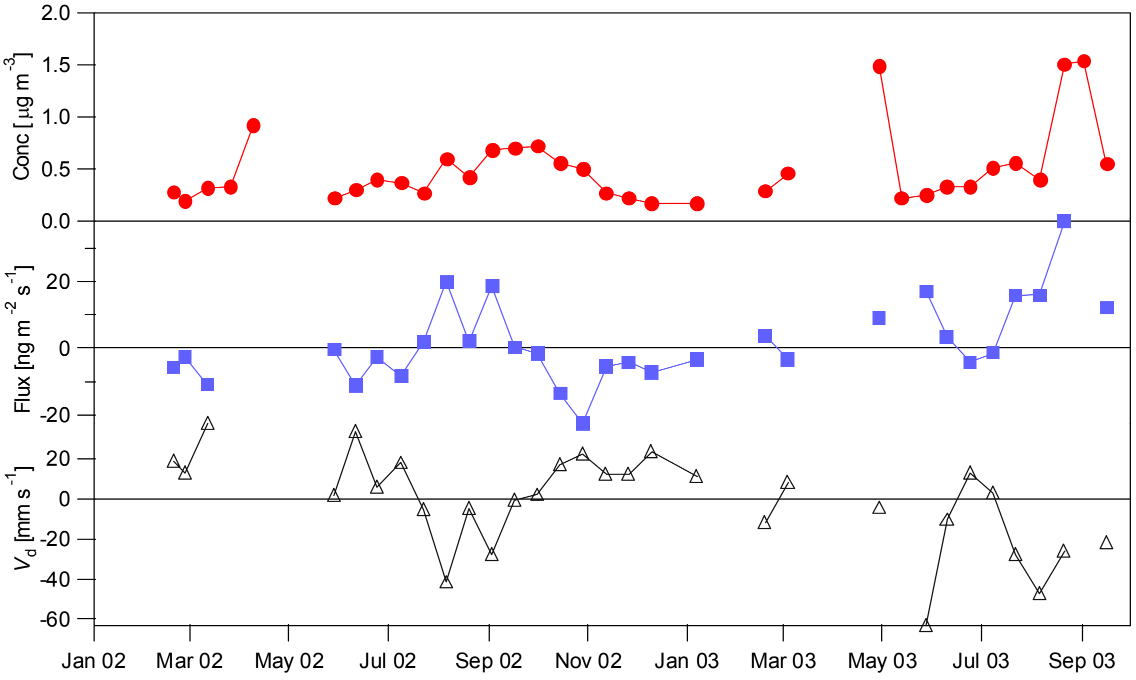


Figure 5.16: Plynlimon TAG results.

At Easter Bush the TAG system was compared against a 3-point AMANDA gradient system. The AMANDA inlets were positioned at heights of approximately 0.5m, 0.8m, and 2.0m, with the inlets facing NW. At Easter Bush, the TAG system consisted of 5 sensors, placed at 2.38, 1.42, 0.84, 0.50, and 0.30m above ground. Dates The AMANDA data output was collected in 15min intervals. As with the TAG systems at Auchencorth Moss and Plynlimon, the airpump of the TAG was switched off when very stable atmospheric conditions were detected. The meteorological data provided by the TAG system were collected every 30 minutes, regardless if the pump was active or not.

Two alternative estimates of the fortnightly fluxes were derived from the AMANDA gradients: a straight average of the flux provides the best estimate of the true exchange. An alternative estimate was derived to mimic the conditional sampling of the TAG system, and should provide better comparability between the two systems. To obtain this estimate, the TAG data were first interpolated to provide 15 min intervals. These data were then used to remove from the AMANDA time-series periods, during which the TAG airpump had been switched off. The remaining data were averaged according to the TAG sampling periods. Both estimates are plotted alongside the TAG data in Figure 5.17.

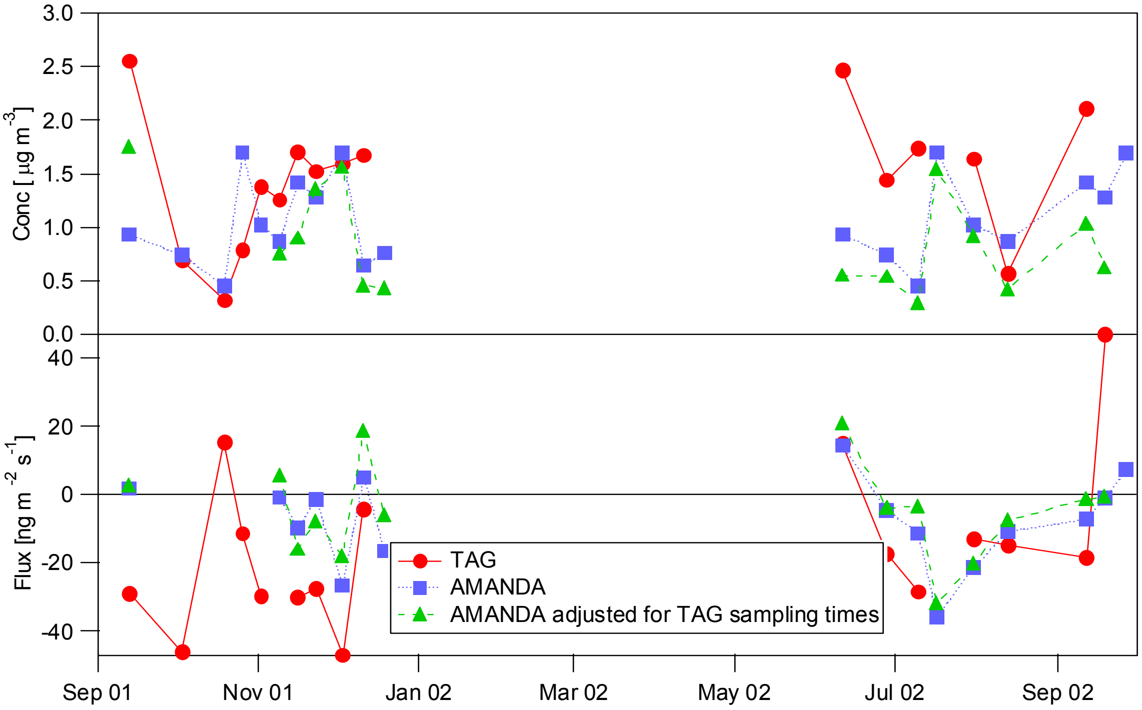


Figure 5.17: Easter Bush TAG results.

The removal of very stable (night-time) periods from the AMANDA average tended to decrease both concentrations and deposition (or increase emission) slightly. This is expected to be a general feature of the TAG sampling approach. Scatter plots provide a clearer picture of the correlation between the TAG measurements and the adjusted AMANDA measurements (Fig. 5.18). The regression analysis of TAG *vs*. unadjusted AMANDA flux revealed a realationship of y = 1.33x -3.61 (r^2 = 0.29). Once the AMANDA data had been TAG-adjusted, the relationship was y= 0.94x – 11.13 (r^2 = 0.24), with a slope close to 1 but overall smaller values derived by the TAG.

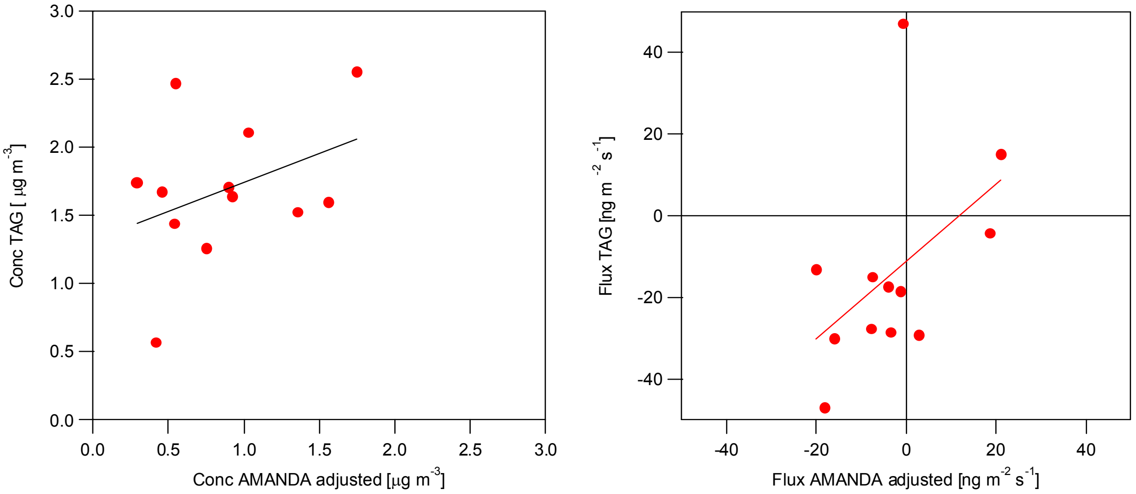


Figure 5.18: Correlations of Easter Bush TAG results versus adjusted AMANDA data for (a) concentrations and (b) fluxes.

It should be noted that the wet conditions during 2002 provided challenges for the operation of the AMANDA system, resulting in poor data coverage for some TAG runs. Hence the absolute accuracy of the TAG approach is currently difficult to assess. The greater number of measurement heights at Easter Bush (5) compared with the semi-natural field sites (3) enables a more rigorous analysis of the log-normality of the vertical concentration profiles, which provides an estimate of the error. In addition, individual outlier, e.g. due to sample contamination or pump malfunctioning, may be identified and eliminated. Following these first long-term tests of the TAG approach a minimum number of 5 sampling heights is therefore recommended.

5.3.4. MEASUREMENTS IN THE EUROPEAN CONTEXT.

Through participation of CEH in the EU GRAMINAE project, the measurements at Easter Bush could be interpreted across with similar measurements made along a transect, spanning a wide range of climates and agricultural management regimes. In addition to Easter Bush, continuous measurements of ammonia exchange were made in 5 other countries across the GRAMINAE transect of increasing continentality. Each of the countries either made measurements over contrasting intensive and extensive semi-natural grasslands or were able to analyze existing measurements. For the Scottish comparison existing data were re-analyzed for the semi-natural moorland/grassland at Auchencorth Moss. The measurement techniques employed consisted of either high temporal resolution data (15 min fluxes) with AMANDA or mini-WEDD gradient systems or the TAG low-cost methods for measuring fluxes with longer time resolution (weekly or fortnightly).

Semi-natural grasslands are most easy to compare as management intervention by fertilization and application of manures is avoided. The Scottish and Hungarian sites showed net deposition, while the Dutch and Greek sites showed net NH_3 emission. However, although semi-natural, the Dutch semi-natural grassland is in fact grazed by a large number of geese, as well as some horses, providing a major nitrogen input to the site. It is not clear, why the unfertilised Greek grassland should emit NH_3. Although the annual figure is noted as rather uncertain and not for a full year, both the TAG and PFS systems recorded emission during winter (Figure 5.8). It is possible that this is related to the use of this grassland as open rangeland during this period.

Comparison of the Hungarian and Scottish sites shows that, while the deposition flux at the Hungarian site was nearly double that at the Scottish site, the average deposition velocity was only around one third of that at the Scottish site. In this comparison of two unfertilised semi-natural grasslands, with minimal grazing, the effect of climate becomes apparent. In Scotland windspeeds are higher (leading to larger maximum possible deposition velocities, V_{max}), while the canopy is much more humid allowing for more effective deposition to leaf surfaces. In addition, frozen conditions in winter would limit deposition rates. This difference in average deposition velocity is therefore consistent with the initial GRAMINAE hypothesis of the effect of continentality on NH_3 exchange. As a result, NH_3 is expected to have a longer atmospheric residence time in continental than oceanic climates.

It is useful to view the average fluxes measured at all the GRAMINAE sites graphically in relation to fertilizer N input and average NH_3 air concentrations (Figure 5.19). Figure 5.19A shows how there is little clear relationship between fertilizer N inputs and average NH_3 flux. However, in general it can be stated that the highest NH_3 emissions per unit of N input occur from fields with organic manure application (NL) and grazing (NL, GR), while the lowest NH_3 emissions per unit N input occur from sites where N addition is either by fixation through clover (CH) and mineral fertilizer application (UK, FR). The exception to this pattern is the high NH_3 emission from the fertilized Hungarian grassland, and this is an issue that warrants further investigation.

Although there are uncertainties in some of the annual estimates of NH_3 exchange (some of the estimates are based on limited available data), it is encouraging to observe a clear relationship between average NH_3 flux and NH_3 air concentration (Figure 5.19B). For sites where deposition dominates, flux is a function of NH_3 concentration, with deposition proportional to concentration. However, where emission occurs, the NH_3 concentration is dependent on the emission itself, and this can be seen in the comparison between sites. The existence of this relationship for the GRAMINAE sites that are net NH_3 emitters indicates that these grasslands provide the main control on NH_3 concentrations above the site, rather than other local sources.

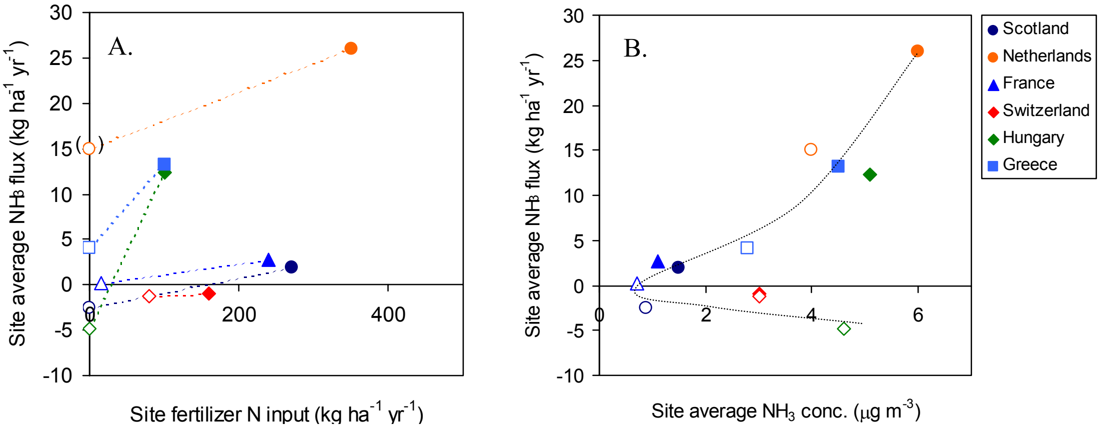


Figure 5.19. Estimated average NH_3 fluxes (kg N ha^{-1} yr^{-1}) in relation to site (mineral + organic) fertilizer N input and in relation to site average NH_3 air concentration. Filled and open symbols represent the high N and low N input GRAMINAE grasslands, respectively. The Scottish sites are Easter Bush (intensive agricultural, high N) and Auchencorth Moss (semi-natural, low N).Although no fertilizer is added to the low-N site in the Netherlands, this receives additional N input from geese.

5.3.5. INTERNATIONAL INTER-COMPARISON OF AMMONIA FLUX MEASUREMENTS AT BRAUNSCHWEIG

GRAMINAE and BIATEX-2 provided the framework for a major NH_3 campaign, which took place in May and June 2000, at the Federal Agricultural Research Centre at Braunschweig, Germany. It provided both an instrument intercomparison and an integrated approach to the detailed study of NH_3 with grassland, which, in complexity, reached far beyond the possibilities of a single group or country. In particular, it provided the unique opportunity to test the UK flux measurement equipment against most of Europe's major NH_3 labs and to compare the different flux measurement approaches available at the time (gradient method, REA, surface dispersion modelling). In addition to the 7 GRAMINAE partners, contributions were made by another 5 non-GRAMINAE BIATEX-2 groups, including the host institute, the Institute for Tropospheric Research, Leipzig (D), and the Universities of Berne (CH), Bonn (D) and Lancaster (UK). A total of 57 scientists visited the field site during the field campaign.

5.3.6. INTER-COMPARISON OF NET AMMONIA FLUXES BY GRADIENT METHODS AND EFFECTS OF MANAGEMENT

Ammonia fluxes were measured by the aerodynamic gradient method at 15-minute time resolution by 4 different groups at two locations. At Site 1 two groups (FRI and FAL-D) measured fluxes using AMANDA's and 1 group (FAL-CH) used mini-WEDD instrumentation. In addition, NH_3 exchange measurements were made with AMANDA by CEH at Site 2 (200 m downwind of Site 1) to identify and quantify any advection of NH_3 from the nearby farm (see Loubet *et al.*, 2002b). The GRAMINAE Integrated Experiment has provided the first such major inter-comparison of gradient systems and these datasets reflect a large effort by the different groups. The NH_3 fluxes from these 4 instruments were filtered for periods of malfunctioning, calibration and obstruction in particular wind sectors and the results of the comparison are shown in Figure 5.20 for different key periods. Considering that NH_3 fluxes are notoriously difficult to measure, the agreement reached between the 4 techniques (all run by different operating teams) is encouraging. There are some periods of very close agreement, such as 6 & 7/6/2000 whilst other days such as 8/6/2000 do show a discrepancy between the estimates.

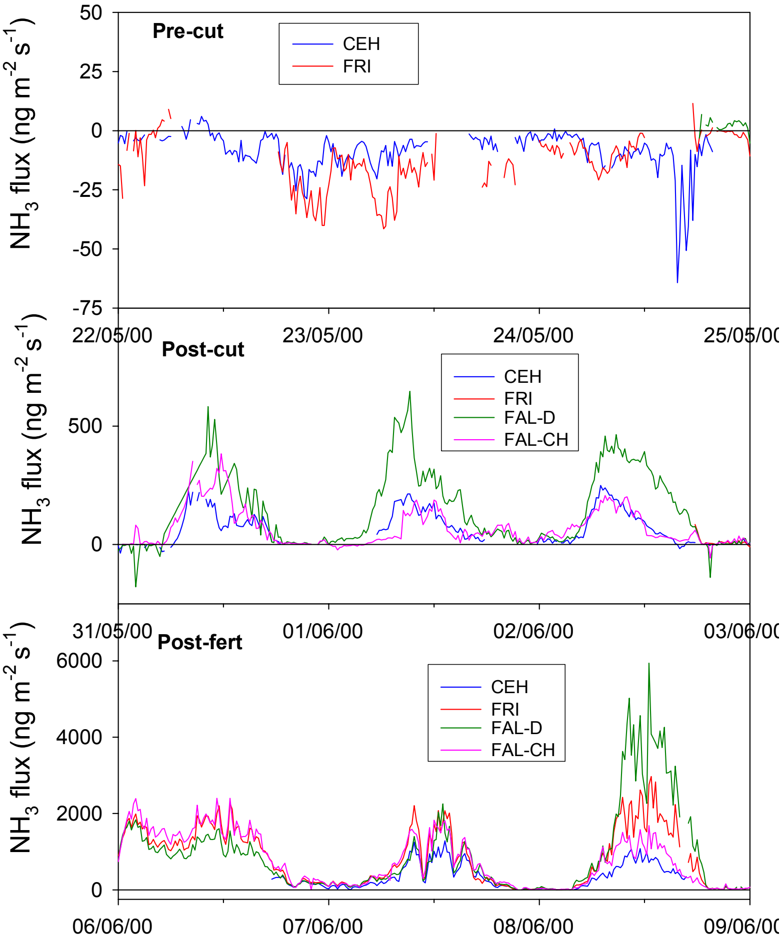


Figure 5.20. Example of NH_3 fluxes from the 4 different systems, pre-cutting, post-cutting and post-fertilising.

A mean gradient flux and concentration were calculated from the mean of all 4 individual fluxes and concentrations when available. Having 4 different systems ensured exceptional data coverage of the mean gradient estimate (98% when considering all data and 69% when considering those data which pass strict micrometeorological criteria) and produced a robust final dataset of the fluxes and concentrations (Figure 5.21).

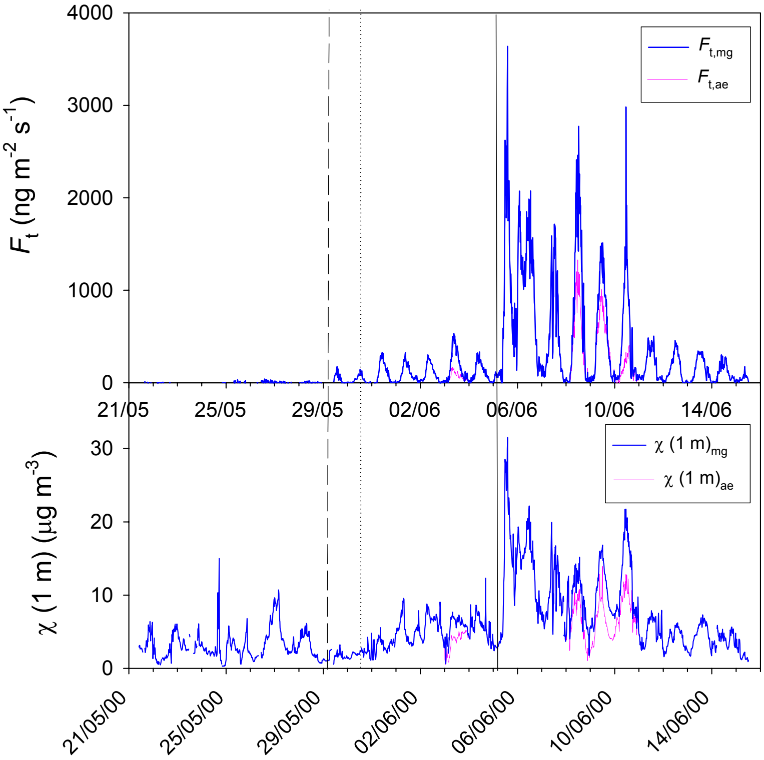


Figure 5.21. Mean gradient estimate of the net NH_3 flux ($F_{t,mg}$) and χ(1 m) showing response to management activities. For comparison an alternative estimate ($F_{t,ae}$) is also shown for periods where there was doubt in the results of some analyzers. Vertical lines indicate cutting (dashed line), removal of the grass from the field (dotted line) and $NH_4^+NO_3^-$ fertilisation (solid line).

Figure 5.21 demonstrates the strong response of the intensive grassland to the management activities of cutting and fertilising. Similarly to the results from the CEH Easter Bush site, the NH_3 exchange changes from small deposition to significant emission after cutting and these enhanced emissions continue for some days before the expected larger emissions after fertilisation. After fertilisation it is difficult to separate out the contribution of direct fertiliser emission and indirect emission from the plants themselves using the micrometeorological flux measurements alone. Cuvette experiments and modelling activities can provide additional insight into this partition.

5.3.7. EVALUATION OF RELAXED EDDY ACCUMULATION METHODS FOR AMMONIA

In Braunschweig, an improved version of the CEH REA system was used tested in the field for the first time, simultaneously with three other GRAMINAE NH_3 REA systems, and a fourth system, developed by RISO (DK). Despite some individual less certain days, the average of up to five gradient systems (see previous section) provided a benchmark estimate of the NH_3 exchange of a robustness, which could not have been achieved at a national sampling site.

Figure 5.22 shows the comparison of the concentration and flux time series derived with the four REA systems with the gradient estimates. As with the FIDES modelling

(Section 5.2.6), the REA measurements lend support to the lower gradient estimate on 3, 8, 9 and 10 June, suggesting that the two gradient systems that were reading high were at error.

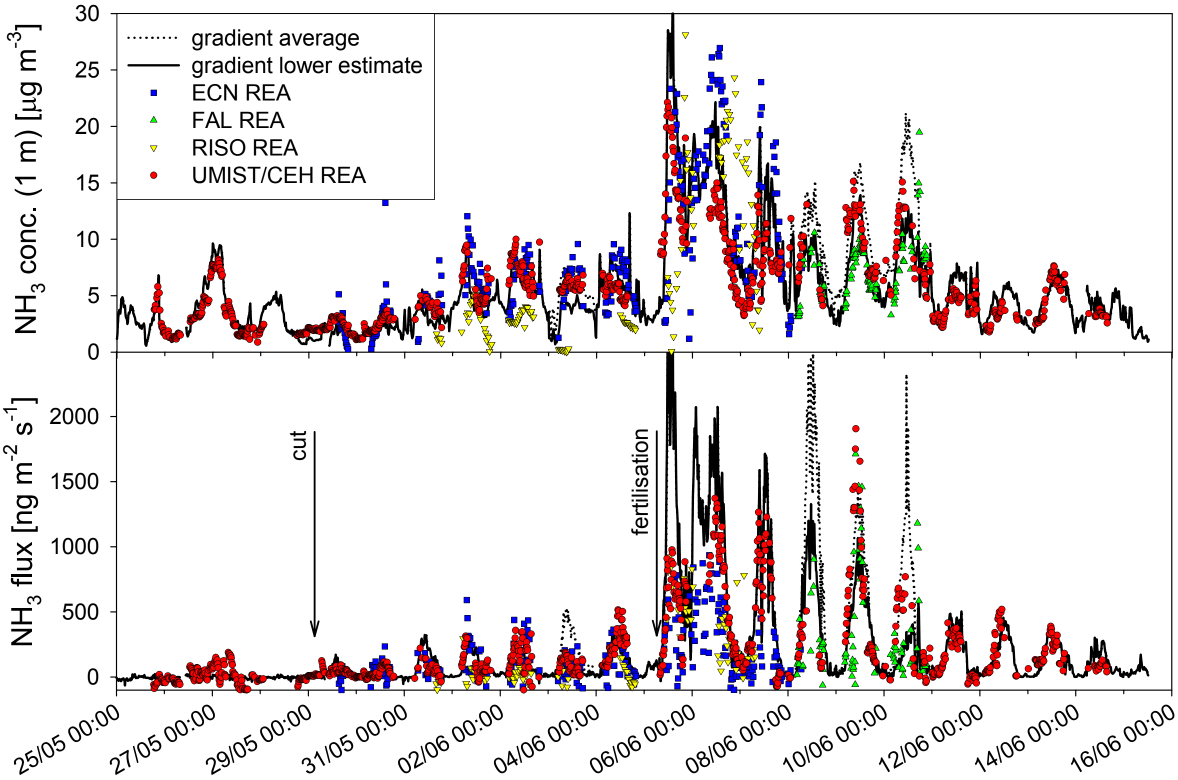


Figure 5.22. The complete time series of the concentration (normalised for z-d = 1 m) and flux measurements with the four REA systems in comparison with the average and the lower gradient estimate. Fluxes started to increase on 29 May after cutting. Fertilisation on 5 June led to high fluxes, which decreased with time.

Scatter plots of the correlation between REA fluxes and the lower gradient estimate is shown in Figure 5.23. On average, the REA systems underestimate the flux by 10 to 45 % compared with the gradient estimate, for high fluxes. Possible explanations include:

(a) the underestimation in fluxes is partly a consequence of the underestimation in the concentrations;

(b) although delay times of switching, sampling and analysis were accounted for in the systems, the limited time-response of the scrubbers themselves tends to even out concentration peaks, resulting in smaller fluxes;

(c) the REA approach potentially suffers the same flux losses as eddy-covariance, e.g. due to sensor separation and inadequate sampling frequency. This may have in particular affected the FAL system which was operated at a lower height of 1.09 m;

(d) if concentrations did not completely equilibrate during the referencing mode (arbitrary switching, independent of w), which was used to correct for small systematic differences between the channels, this may have reduced the flux.

(e) investigations have yet to be carried out to show that the empirical REA coefficient (β) remains unaffected by chemistry.

The REA systems performed best in the intermediate flux range (100 to 1500 ng m^{-2} s^{-1}). At higher concentration, significant curvature and underestimation of the flux relative to the gradient approach, was observed, which may have been caused by limited capture by the scrubbers at high air temperatures of up to 36 °C. By contrast, at lower fluxes the REA systems showed an increasing amount of scatter. In the REA approach concentration differences of often < 2 % have to be resolved if the fluxes are small. Variation in inlet capture efficiency, liquid flow rates and temperature effects on conductivity measurements can be of similar magnitude, and provide an intrinsic limitation for the precision of wet chemistry systems for NH_3. At a time resolution of 15 min. the accuracy of the CEH/UMIST system was in the region of ± 20 % for fluxes >500 ng m^{-2} s^{-1}, and ± 100 ng m^{-s} s^{-1} for smaller fluxes. Although not dissimilar to the gradient inter-comparison, this accuracy is insufficient to quantify vertical flux divergence. The results demonstrate again the difficulties involved in measuring ammonia exchange fluxes accurately. There appear to be intrinsic limitations with the wet chemistry approach and in the future spectroscopical analysis methods such as TDLAS (Zahniser *et al.*, 1996; Warland *et al.*, 2001) and mass spectrometry (Shaw *et al.*, 1998; Nowak *et al.*, 2002) should be explored.

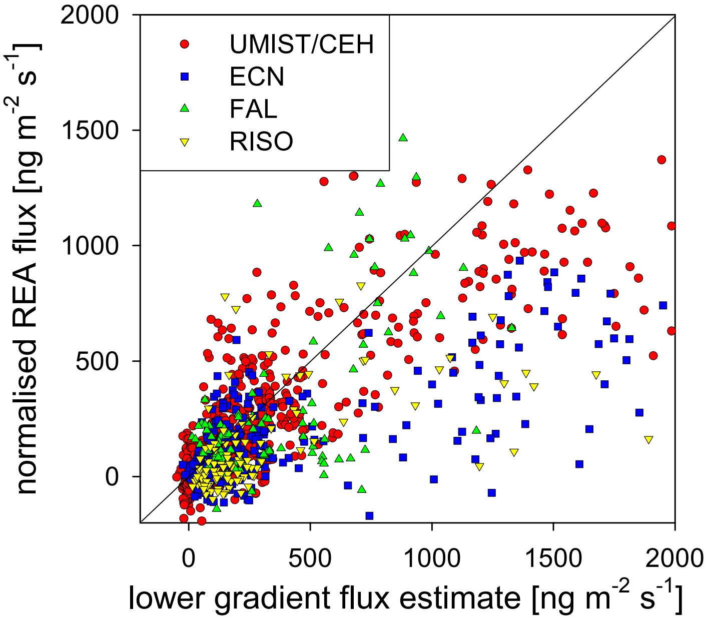


Figure 5.23. Scatter plot of the REA fluxes against the lower gradient estimate. The REA approach underestimated the flux compared with the gradient approach on average by 10 to 45 %.

5.3.8. NOVEL DETERMINATION OF AMMONIA FLUXES NEAR-SOURCE PLUME DISPERSION

The results of the application of the FIDES model to determine NH_3 fluxes with the grassland are shown in Figure 5.24. For this analysis, the mean estimate of measured NH_3 concentrations 1 m above the canopy was applied together with the background NH_3 concentration at 47 m, measured by CEH using at automated rotating wet batch denuder (Keuken *et al.*, 1988). Figure 5.24 shows the model estimate of the ground surface emission potential ($\chi(z_o)$), although it should be noted that, because of the laminar boundary layer resistance (R_b) and various canopy resistances (e.g. R_s, R_{ac}), the actual emission potential would be larger than this. Hence following cutting the ammonia emission potential exceeds values of 40 µg m^{-3}, while after fertilization peak values exceed 100-300 µg m^{-3}.

The most impressive finding of this method is the very close agreement with the average of the flux gradient measurements. This indicates how the concentration enhancement above background is directly a consequence of the surface flux, and can be used as a robust measurement technique for determining NH_3 fluxes. The results also help to clarify the debate over the best gradient measurements for the days where there was a wide divergence of gradient estimates. The near source plume dispersion method indicates the large apparent NH_3 emission on 8 June is too large to be consistent with the concentration enhancement at 1 m. Aside from providing a new measurement method, this result is therefore helpful to clarify the best measurement data for application to the models.

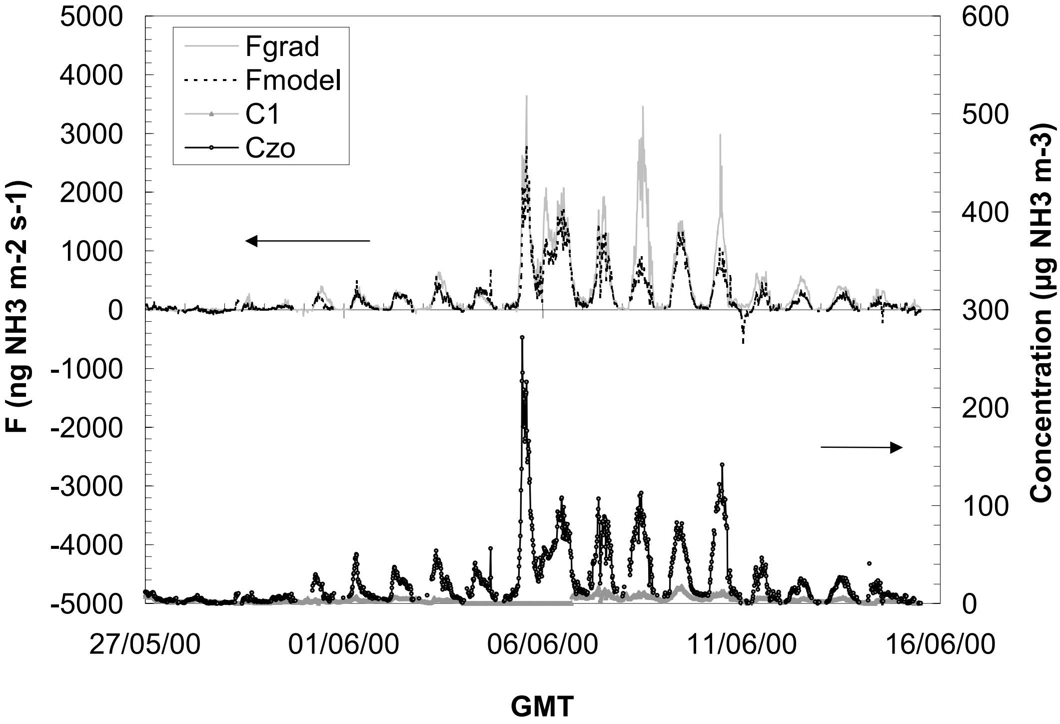


Figure 5.24. Comparison of the net NH_3 flux over the grassland at Braunschweig during the GRAMINAE Integrated Experiment using the FIDES near-source dispersion method (F_{model}) and the aerodynamic gradient method (F_{grad}, grey line). Also shown is the comparison of the measured average NH_3 concentration at 1 m (C1) and the modelled surface NH_3 concentration at z_o (Czo) (bold black line). The main uncertainties in F_{model} are the estimate of C1 (bold grey line) and background NH_3 concentration (dotted black line), while the main uncertainties in F_{grad} are the measured estimates of the vertical NH_3 concentration profile.

5.4. Interpretation and interactions of ammonia fluxes

5.4.1. INTERACTIONS OF THE FLUXES OF AMMONIA, ACIDS AND ATMOSPHERIC PARTICLES.

Chemical production or destruction of a tracer during its emission or deposition process, results in a change of its flux with height (vertical flux divergence), which needs to be accounted for if the true surface exchange flux is derived from micrometeorological flux measurements made well above the ground. Ammonia reacts reversibly with HNO_3 and HCl in the atmosphere, forming the associated aerosol components, NH_4NO_3 and NH_4Cl. Tests to estimate if chemical conversion is sufficient to modify exchange fluxes include: (a) assessment of the deviation from thermodynamic equilibrium, (b) calculation of chemical time-scales from the surface area provided by the particle loading, and (c) measurement of exchange rates of acids and aerosols and comparison with expected rates. HNO_3 and HCl are usually expected to deposition at the maximum rate permitted by turbulence (V_{max}). Deviations indicate chemical processes at soil or leaf surfaces or within the air. For particles deposition rates are more difficult to predict in advance. Information on nucleation mode particles (< 0.1 µm) is particularly sparse as these cannot be sized with available optical methods. At Braunschweig, the dependence of the deposition rate of small particles, measured using a condensation particle counter (CPC), on friction velocity (u_*) before and after the cut were similar suggesting that the deposition rate of nucleation mode particles is insensitive to surface roughness. By contrast, a compilation of size-resolved particle flux measurements of accumulation mode particles in Braunschweig and during recent campaigns shows a strong increase with surface roughness (z_0), which, for the size-range 0.1 to 0.2 µm, follows a logarithmic relationship.

Figure 5.25 shows the full time-series of the CPC particle flux measurements at Braunschweig. Before the cut the flux is on average deposition (cf. Figure 5.21). The management activities (cutting, turning, lifting), with agricultural machinery on the field induced periods of emissions, although the micrometeorological approaches used here cannot be expected to quantify these spatially inhomogeneous emissions reliably.

Persistent apparent particle emissions, following a diurnal cycle, were observed after fertiliser application. These were correlated with the NH_3 emission flux (Figure 5.25B). VOC emissions, which should have been strongest directly after the cut, were eliminated as particle precursors through selected concentration and flux measurements by REA using adsorption tubes. Particles, freshly nucleated at the field site would have grown too slowly to be detected by the CPC with a lower cut-off of 11 nm and continuous measurements of the aerosol size-distribution using a differential mobility particle sizer (DMPS) did not indicate large concentration of nucleation mode particles. The apparent emission flux is therefore almost certainly caused by the condensation of NH_3, emitted directly from fertiliser pellets and, later on, mitigated by the canopy, on the surface of pre-existing particles during their deposition. This leads to a larger number of particles > 11 nm at lower heights, which is detected as an emission flux by the CPC EC setup. This process causes a mass emission flux, at the same time as, in the absence of new particle formation, the physical number flux remains downward. The role of HNO_3 in the process is less certain. The reduced deposition rate of HNO_3 after fertilisation suggests that the NH_4NO_3 pellets induced a ‘chemical compensation point’, which would have maintained a considerable HNO_3 concentration within the canopy. The aerosol growth rates derived from the measurements at Elspeet were considerably larger than any growth rates reported for natural environments, including coastal environments and Boreal forests.

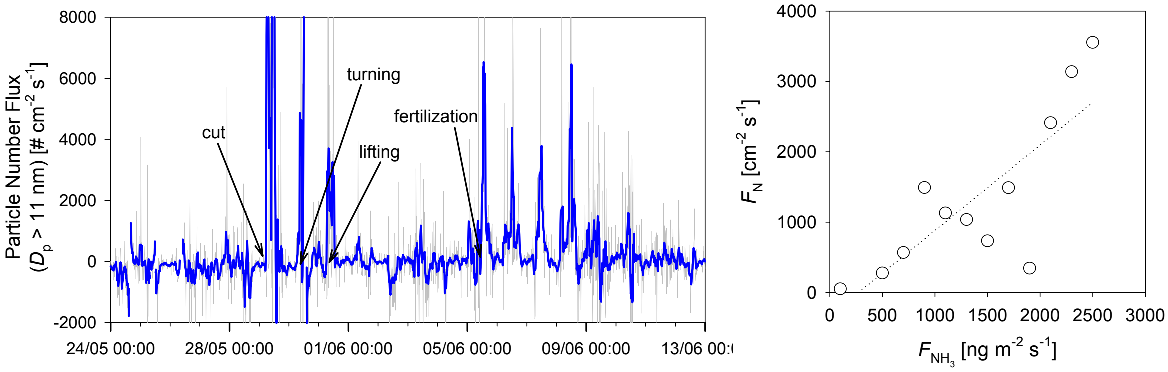


Figure 5.25. Time-series of the CPC flux measurements of the total particle flux (11 nm – 2 μm) in relation to management activity.

The opposite effect, aerosol evaporation was observed during an earlier measurement campaign at the Dutch semi-natural heathland ‘Elspeetsche Veld’. Here, both NH_3 and the atmospheric acids tended to be deposited to the vegetation, resulting in decreased concentrations close to the ground. While gas / aerosol equilibrium appeared to be established well above the ground, the gas-phase depletion close to the vegetation resulted in an evaporation potential for NH_4NO_3 and NH_4Cl aerosols, which was further exacerbated by high canopy temperatures. It is likely that both previously deposited particles and leaf surfaces and airborne particles underwent the same mechanism. Observed effects included (a) reduced deposition velocities of HNO_3 and HCl, (b) apparent high deposition velocities of NH_4^+ aerosol, and (c) complex bi-directional behaviour of size-segregated particle number fluxes measured by eddy-covariance using an optical aerosol spectrometer. It was concluded that this aerosol evaporation results in an underestimation of the NH_3 uptake by the surface of 15% and affects parameterisations of particle deposition velocities derived from eddy-covariance flux measurements. A set of three scientific papers on this earlier campaign were finalized as part of the Acid Deposition Processes project (Nemitz *et al.*, 2004a, b; Nemitz and Sutton, 2004).

5.5. Development of process based models of ammonia exchange

5.5.1. BI-DIRECTIONAL RESISTANCE MODELS OF AMMONIA EXCHANGE

In the earliest models of NH_3 exchange with vegetation it was assumed that uptake or release occurs solely through plant stomata (e.g. Farquhar *et al.* 1980). In contrast, the usual models of pollutant 'dry deposition' (e.g. Erisman *et al.* 1994), were not mechanistically suitable for describing emissions. Moreover, when the deposition models were applied to consider NH_3 fluxes to semi-natural vegetation, it was shown that exchange is often dominated in field conditions by uptake onto plant cuticles rather than through stomata (Sutton *et al.* 1993a). Both these model approaches applied a resistance analysis, separating the atmospheric turbulent resistance (R_a) and the quasi-laminar boundary resistance (R_b) from resistances at the surface. The stomatal exchange model may be expressed as:

$$F_t = (\chi_s - \chi_a)/(R_a + R_b + R_s) \qquad (2)$$

while the dry deposition model is expressed most simply as:

$$F_t = -\chi_a/(R_a + R_b + R_c) \qquad (3)$$

where F_t is the net flux (deposition is denoted as negative), χ_a is NH_3 concentration at a reference height above the surface, R_s is stomatal resistance and R_c is the canopy or surface resistance. The last is a compound term resulting from several component uptake pathways acting in parallel, such as through stomata, to leaf surfaces and to bare soil.

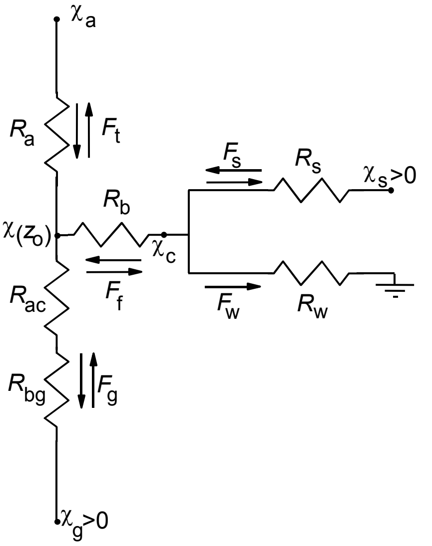


Figure 5.26. Diagram of the 2-layer canopy compensation point model: χ_a is the NH_3 air concentration; F_t, net flux; R_a, aerodynamic resistance; R_b, quasi-laminar boundary layer resistance; R_w, cuticular resistance; R_s, stomatal resistance; R_{ac}, in-canopy aerodynamic resistance and R_{bg}, ground boundary layer resistance, see Nemitz *et al.*, (2001b) for more details.

In response to the limitations of these models Sutton *et al.* (1995b) developed a revised resistance model for NH_3 exchange. The 'canopy compensation point' model makes the distinction between the potential for exchange with stomata (χ_s) and the potential for exchange with the canopy as a whole, the canopy compensation point (χ_c), as shown in Figure 5.1a. The value of χ_c may be estimated as:

$$\chi_c = \frac{\chi_s / R_s + \chi_a / (R_a + R_b)}{(R_a + R_b)^{-1} + R_s^{-1} + R_w^{-1}} \qquad (4)$$

from which the net flux is calculated:

$$F_t = (\chi_c - \chi_a)/(R_a + R_b) \qquad (5)$$

where R_w is the resistance for deposition of NH_3 to plant surfaces.

This model has been shown to be able to reproduce bi-directional NH_3 fluxes with some success (e.g. Sutton *et al.* 1995a,b, 1998, Flechard *et al.* 1999). The model, nevertheless, still represents a simplified treatment of the exchange process. In some situations decomposing leaf litter under the canopy may be a source, with some of the emitted NH_3 contributing to the net flux above the canopy. In addition, reproductive tissues at the top of the canopy may have larger χ_s than the foliage. To deal with these cases Nemitz *et al.* (2000b) have developed 2-layer and 3-layer χ_c models. While the 3-layer model is most realistic for some complex canopies, it is generally considered that the 2-layer model provides an appropriate balance between detail and ease of applicability. The 2-layer approach (Figure 5.26) is therefore that recommended for generalization purposes (Nemitz *et al.* 2001b).

The value of R_w is generally parametrized on the basis of relative humidity at the canopy surface, with this increasing exponentially at lower relative humidity (Sutton *et al.* 1995). However, the response function is also dependent on chemistry at the leaf surface, for example due to the presence of SO_2, HNO_3 or base cations (Sutton *et al.* 1993a, Wyers and Erisman 1998, Flechard *et al.* 1999). R_w also represents a simplified description of cuticular uptake, since both adsorption and desorption may occur. More detailed approaches consider the dynamic behaviour of the plant surfaces as a capacitor allowing adsorption/desorption (Sutton *et al.* 1998), as well as treat the full interaction with other chemical species (Flechard *et al.* 1999).

The value of χ_s may be parametrized simply by applying the solubility and dissociation equilibria (Sutton *et al.* 1994, Nemitz *et al.* 2000) such that:

$$\chi_s = \frac{161500}{(T_s - 273.15)} \exp^{\left(-\frac{10380}{T_s - 273.15}\right)} \Gamma \tag{6}$$

where as stated earlier $\Gamma = [NH_4^+]/[H^+]$ in the apoplast, and T_s is the temperature of the canopy in ºC. The temperature function is substantial, and has the effect of doubling χ_s for every 5 ºC increase given a constant value of Γ. A similar relationship applies to χ_{ground}, though in this case, Γ may be a result of either soil surface or litter sources.

Examples of the application of the two-layer compensation point model are shown in Figures 5.27 and 5.28. In Figure 5.27, the measured NH_3 fluxes are compared with modelled estimates for the Easter Bush site before and after the first cut of the grassland in 1999. Emissions did not increase immediately after application, probably because of dry weather conditions, as the presence of some water mobilizes the N. By contrast, the very wet conditions in the preceding week, reduced the initial emissions after cutting as with ample supply of water the ammonium stays in solution. The normal increase in NH_3 emissions following cutting therefore took several days to appear. These features are reproduced in the model estimates. The values of $\Gamma_{stomata}$ and Γ_{ground} are fitted with simplified smoothed functions (Figure 5.28), which is helpful to demonstrate the robustness of the model. The increased emissions following cutting and fertilization are attributed in the model to the increased ammonium in leaf tissues, while soil emissions last around four days.

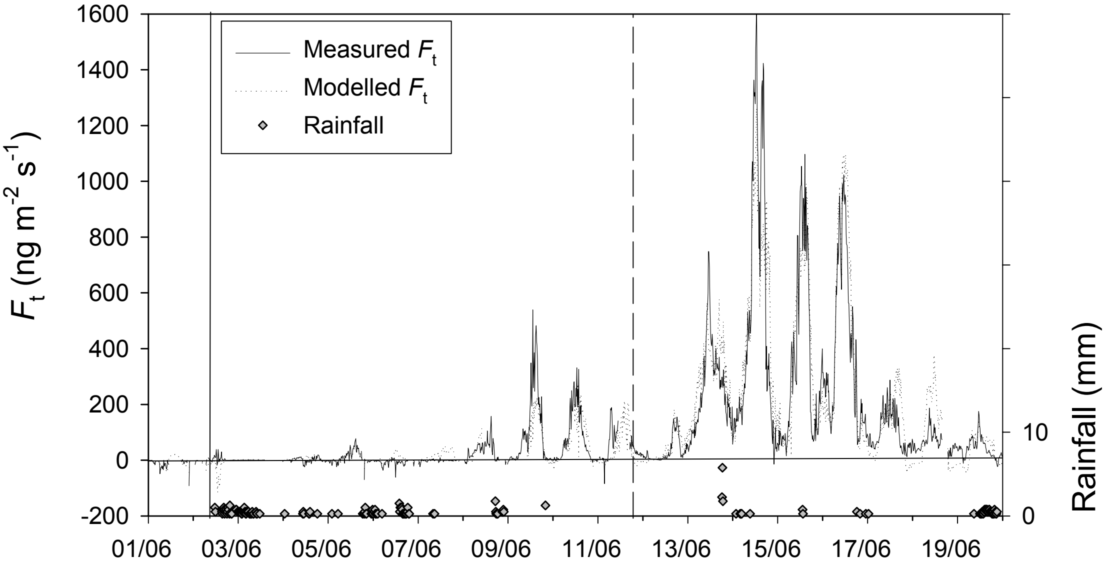


Figure 5.27. Measured and modelled net flux (F_t) at Easter Bush plus rainfall for the period 1-20/6/99, vertical lines indicate cutting (solid line) on 2/6/99 and NH_4NO_3 fertilisation (dashed line) on 11/6/99.

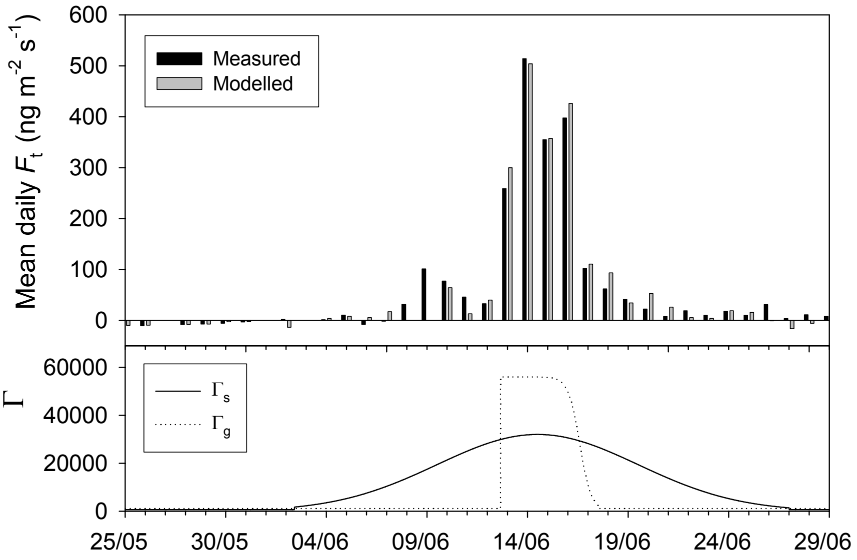


Figure 5.28. Measured and modelled mean daily net flux at Easter Bush plus the time-dependent functions of foliar (Γ_s) and ground layer (Γ_g) emission potential, measurements and model data are only shown for daily data capture > 70%.

As a contrast to these approaches, work in GRAMINAE has also worked further with the dynamic compensation point model of Sutton *et al.* (1998) that allows for cuticular adsorption and desorption (Figure 5.1b). While this model proves very useful to explain the exchange processes in more detail, as does the full chemistry version of the model developed by Flechard *et al.* (1999), the need for small time steps make this model less well suited for general application in other more general dispersion and ecosystem models. As a result, simplified parametrizations of cuticular exchange using R_w provide a reasonable balance between process description and simplicity of implementation.

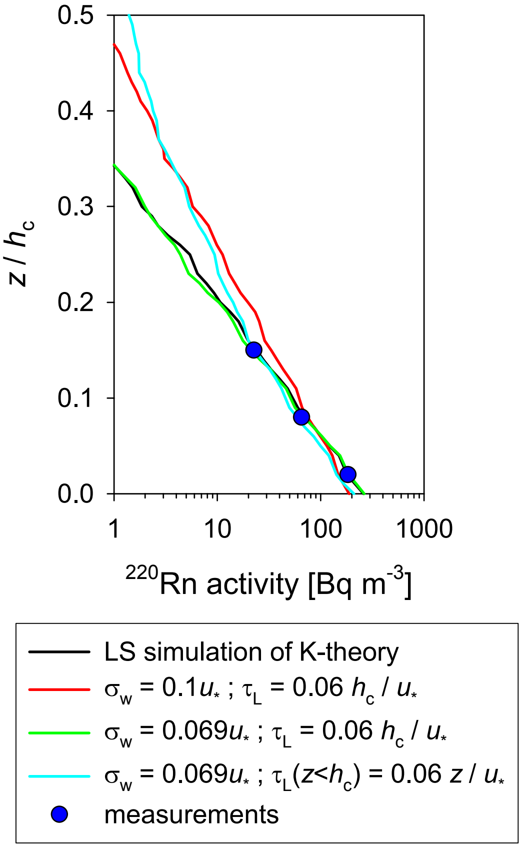


Figure 5.29. Sensitivity analysis of Lagrangian stochastic model results close to the ground to turbulent parameters (σ_w and τ_L) by comparing modelled ^{220}Rn profiles with measurements.

5.5.2. MODELLING WITHIN CANOPY FLUXES OF AMMONIA

Inverse Lagrangian techniques based on near-field-theory and a random walk model can be used to model the vertical distribution of sources and sinks of trace gases. The comparison of the net heat flux above the canopy, derived from in-canopy profiles of temperature, with the micrometeorological flux measurement provides a test for the description of the turbulence in the modelling approaches (e.g. Nemitz *et al.*, 2000b)

At the integrated GRAMINAE experiment at Braunschweig, measurements of activity profiles of ^{220}Rn and ^{222}Rn provided a further test for the Lagrangian approaches and the description of the in-canopy turbulence (Figure 5.29): firstly the K-values derived from the ^{220}Rn tracer methods were verified by the application of a Lagrangian stochastic (LS) model which simulates the *K* approach. Secondly, various parameterisations of σ_w and τ_L close to the ground were applied to assess their effect on the concentration profiles of a tracer that is emitted by the ground. In summary, the results are much less sensitive to the parameterisation of τ_L than of σ_w.

Although the measurements of in-canopy NH_3 profiles at Braunschweig are not without uncertainty, the inverse Lagrangian technique based on Raupach (1989) was applied to derive approximate source / sink distributions of NH_3. An example is shown in Figure 5.30, which demonstrates that the lower canopy acted as a source for NH_3. This was recaptured in the lower part of the mid canopy, with the top canopy being inactive prior to the cut. Indeed very small fluxes were measured before the cut.

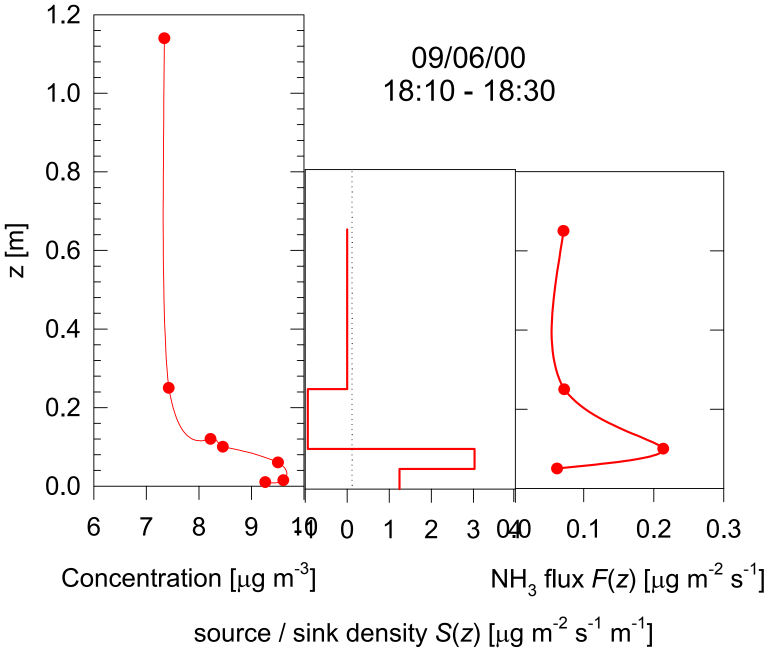


Figure 5.30. Example application of the inverse Lagrangian technique based on near-field theory to derive the vertical source / sink profile in the grassland canopy during the GRAMINAE Integrated Experiment at Braunschweig.

5.5.3. DEVELOPMENT OF A COUPLED DYNAMIC MODEL OF AMMONIA BI-DIRECTIONAL EXCHANGE AND ECOSYSTEM FUNCTIONING.

Two major advances were made in the development of the PASIM model in relation to NH_3 exchange, linked to the dynamic estimation of $\Gamma_{stomata}$ and Γ_{ground}. Until now modelling of NH_3 exchange in dynamic models of ecosystem functioning has been conducted very simply, using for example fixed value inputs or % emissions. Through the additional input of a TMR fellowship, it was possible to extend the GRAMINAE work to further develop the PASIM model to include a functional dependence of NH_3 exchange, providing a mechanistic model that could be applied to the UK measurement site. For this purpose the two-layer model of Nemitz *et al.* (2001b) was built into the PASIM framework. The challenge was then to provide estimate of both $\Gamma_{stomata}$ and Γ_{ground} dependent on ecosystem functioning. In order to treat Γ_{ground}, a multi-layer soil treatment was implemented, using a top layer of ~2 mm thick. Such a shallow layer was necessary in order to simulate soil surface NH_4^+ concentrations and hence emissions. A major uncertainty, however as with all such soil surface NH_4^+ models was the assumptions of pH, and the model was found to work best with soils at pH 6-6.5. For high pH soils, the model over-estimated soil emissions, and this may be because in practice soil pH is less critical at the immediate surface, where pH is controlled by the fertilizer type and litter breakdown processes.

The most challenging development, however, was to develop a means to estimate the time course of $\Gamma_{stomata}$ in relation to grassland functioning. For this purpose, and based on literature review and the GRAMINAE results, it was first hypothesized that there would be a link between $\Gamma_{stomata}$ and the PASIM model estimate of substrate nitrogen (Sutton *et al.* 2001b). This term was found not to respond sufficiently quickly to explain measured NH_3 fluxes. Therefore a more detailed module was constructed, which separated substrate nitrogen into separate apoplastic and symplastic pools (Figure 5.31). With this system, plant uptake of soil N was supplied directly to the apoplast (since this is contiguous with xylem), while the uptake of nitrogen into the cells is an active, energy requiring flux. At the same time, as concentrations of NH_3 are larger in the symplast than apoplast there is a passive flux from the symplast to apoplast. Ammonia fluxes link to the apoplast in the model, while the other inputs and outputs with the symplast are recycling from decaying leaves and incorporation of N into structural plant parts.

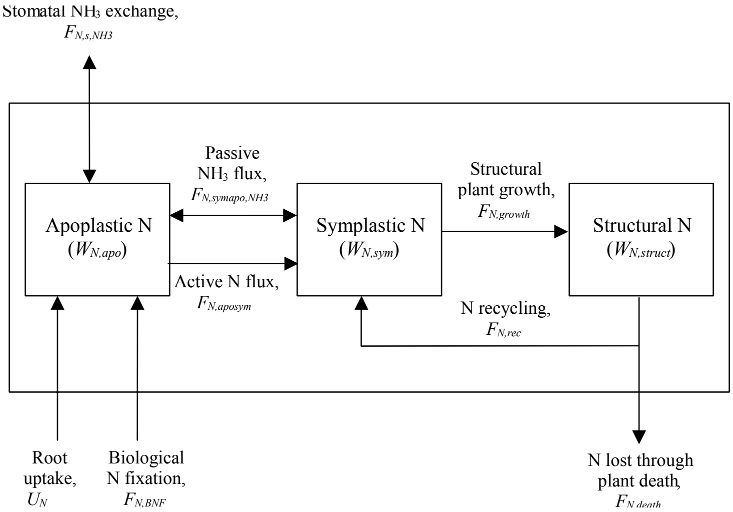


Figure 5.31. Plant N in PASIM is divided among structural N $W_{N,struct}$, apoplastic substrate N $W_{N,apo}$, and symplastic substrate N $W_{N,sym}$. All input/output fluxes of the N pools are shown except for the losses from grazing and cutting (Riedo *et al.*, 1997, 2002).

Example output from PASIM is shown in Figure 5.32 which illustrates the time course of modelled plant N pools for the Easter Bush grassland. Total plant N concentration is the most slowly varying pool, since this is largely made up of structural N. Conversely, the substrate N, which is the sum of both apoplastic and symplastic N varies much more, with significant changes on a daily basis. Even more rapidly changing, however, is the apoplastic N pool, which increases sharply immediately after both cutting and fertilization, and decreases to the previous levels within 3 weeks of cutting. Figure 5.32 also shows the modelled value of $\Gamma_{stomata}$, illustrating how extremely large values are simulated following fertilization and cutting (Riedo *et al.* 2002).

While the PASIM model provides an important heuristic tool to examine processes, it also provides the possibility to address scenarios of changed environmental and management conditions. For example, the flux measurements and modelling show how cutting and fertilization both lead to an increase in NH_3 emissions. Hence fertilizer emissions occur on top of cutting emissions. It could be hypothesized that if more time were allowed between cutting and fertilizing, the plants would be better able to deplete their apoplastic and substrate N concentrations to a level which would mean more of the fertilizer N was absorbed. A second feature is that with a slightly taller canopy, there is more potential for the fertilizer N to be recaptured by the overlying leaves. This issue was investigated in a model study, simply adding a delay of 2 weeks before fertilizer was applied (Figure 5.33). Overall, this led to a reduction of annual net NH_3 emissions by 15%. Such a technique provides an extremely easy abatement measure, demonstrating how small modifications to agricultural practice can have significant effects. While many abatement measures have a significant cost, the only cost of this measure would be the affect on grass dry matter production. In the case of the model simulation there was a 4% reduction in dry matter.

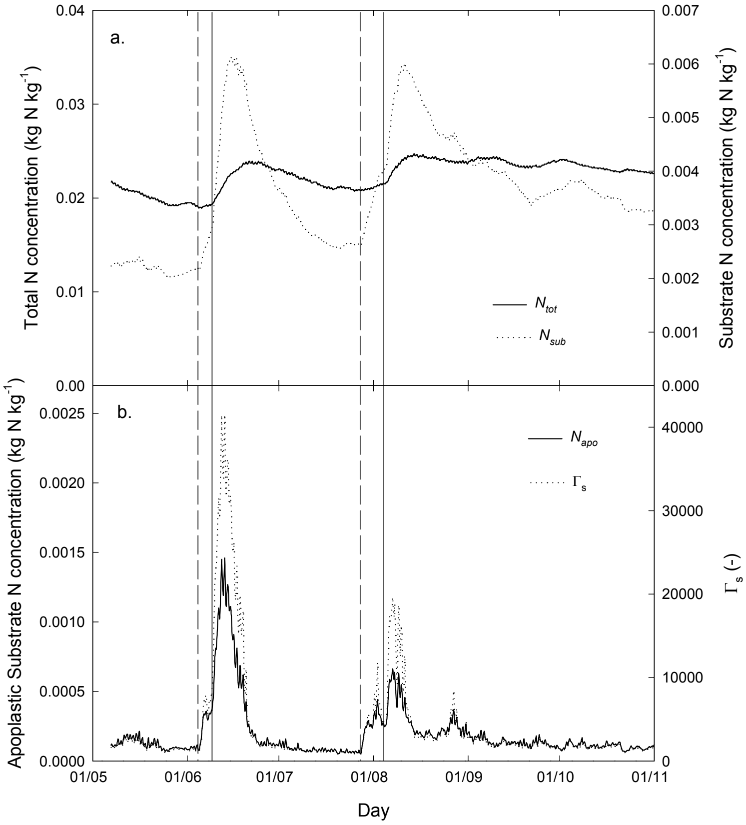


Figure 5.32. Simulated seasonal dynamics of plant N variables and Γ_s for the growing season of 1998 at the Scottish GRAMINAE field site. (a) Plant total N concentration N_{tot}, plant substrate N concentration N_{sub}. (b) Apoplastic substrate N concentration N_{apo}, apoplastic NH_4^+ to H^+ concentration ratio Γ_s. The N concentrations are given as dry weight. Vertical lines indicate cutting (dashed lines) and $NH_4^+NO_3^-$ fertilisation (solid lines).

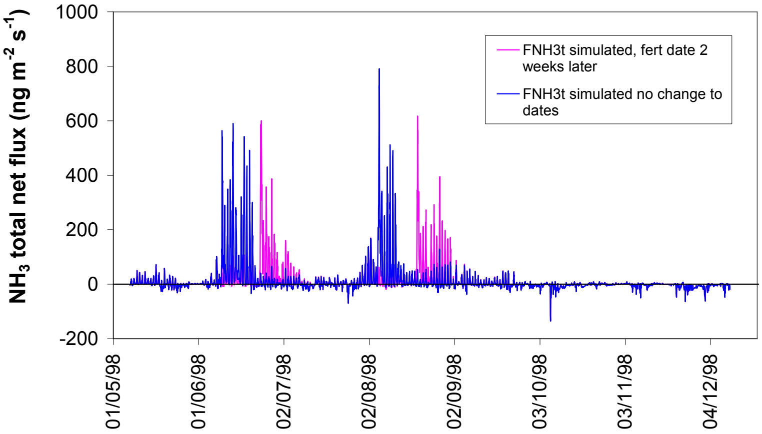


Figure 5.33. Simulated net NH_3 flux at Easter Bush with actual timing of fertilisation and delaying fertilisation date for 2 weeks. Scenario suggests that delaying fertilisation compared with actual practice would lead to a reduction of net annual NH_3 emissions from this site by 15%.

5.6. Discussion and conclusions

5.6.1. STATE OF DEVELOPMENT OF NEW NH_3 FLUX MEASUREMENT TECHNIQUES

Time averaged gradient technique for low-cost long-term dry deposition monitoring

Long-term measurements were also made with the new low-cost TAG technique, at the agricultural field site, two semi-natural grassland UK sites and a site in Greece. The comparison of the TAG with the AMANDA reference system at the agricultural UK site was overall satisfactory. Difficulties in operating the AMANDA system under very wet conditions make it difficult to identify the cause of the residual discrepancy, which may be due to reduced AMANDA data coverage rather than the TAG approach. The comparison of a four channel system (unstable, near-neutral, somewhat stable and off) with a passive sampling system in Greece suggests the active TAG sampling approach to be superior to the passive sampling approach, both conceptually and in reliability. The TAG measurements at the semi-natural sites look very reasonable, especially in comparison with former AMANDA measurements at Auchencorth Moss, which derived similar seasonal cycles and deposition velocities. In particular at the sites where the TAG is the only NH_3 flux instrument, the analysis of the log-normality of measured profiles provides the principal approach for quality control. For this reason, it is recommended that the TAG system be operated with a minimum of five heights. A two-channel system, which switches off in very stable conditions, but accumulates all sample in a single gradient, appears to be sufficient under UK conditions. Very stable conditions are often associated with deposition fluxes and large background concentrations. Simulation of the TAG sampling protocol using the high time resolution AMANDA data from Easter Bush suggests that, at this site, the TAG tends to underestimate concentrations and deposition slightly (< 5 %).

Development of single-height flux measurement approaches

The motivation for the development of relaxed eddy accumulation (REA) and eddy covariance techniques for NH_3 is threefold: first, it enables flux measurements at several individual heights, ideal for quantification of vertical flux divergence caused by advection and chemical interactions. Second, it provides tools that can be applied in logistically challenging situations, such as on aircraft and ship platforms or above urban areas. Finally, eddy-covariance is a direct flux measurement technique, which, unlike gradient techniques and REA, does not rely on empirical parameterisations.

The CEH/UMIST REA system was tested at the UK Easter Bush field site and operated, alongside 3 further REA systems, at the integrated GRAMINAE field campaign at Braunschweig, Germany. It represents an operational system well suited to detect fluxes in the range 100 to 1000 ng m^{-2} s^{-1} and incorporates quality control features (e.g. automatic co-sampling), which cannot easily be implemented in the gradient approach. However, in the REA approach small concentration differences need to be resolved and this limits both the detection limit and accuracy of the approach. This appears to be an intrinsic limitation of wet chemistry sensors and it is unlikely that further progress can be made unless other analytical systems are deployed. In conclusion, the CEH/UMIST REA system may now be applied in logistically demanding situations where reasonably large fluxes can be expected. However, it is currently not suited to the detection of vertical flux divergence.

Eddy-covariance relies on concentration measurements at several Hz. This requires not only a fast analysers, but also a fast inlet system. The CEH TDL-AS approach looks promising, but will probably remain limited to flux measurements at concentrations in excess of 1 ppb. The TDL-AS has a response time of about 0.5 s, which is sufficient for flux measurements above forests, but marginal for smooth vegetation such as grassland. Initial flux measurements at Easter Bush are currently used to quantify potential flux losses. Work is in progress to compare inlets made from various materials to avoid further reduction in the response time of the overall system.

Flux determination through near-scale dispersion modelling

At Braunschweig, an alternative flux estimate was derived using the FIDES dispersion model. Input parameters included a background concentration (measured at 45 m), the concentration measured above the field and standard meteorological parameters (wind speed, wind direction, atmospheric stability and friction velocity) (Loubet *et al*., 2004). This approach yielded surprising good agreement with the gradient measurements (Figure 5.24). It is appears very worthwhile to investigate the potential (and limitations) of this approach further, not just for the determination NH_3 exchange fluxes but as an alternative micrometeorological tool in general.

5.6.2. KEY FINDINGS OF THE FLUX MEASUREMENTS

For the first time, long-term measurements of NH_3 exchange have been made over an intensive agricultural grassland, detailed information for process model development, information on seasonal variations in response to agricultural management and annual budgets. The flux changes greatly with the N status of the grassland: during un-grazed winter periods the grassland acts as a sink for ammonia, before grass cutting induces significant NH_3 emissions, which are further enhanced by fertilizer application a few days after the cut. During grazing periods, the grassland acts as a variable net source. This overall pattern was reconfirmed during measurements at Braunschweig, although at other European sites the magnitude of the individual component fluxes varied with meteorology and N input. At the UK field site the annual emission amounted to 1.9 kg N ha^{-1} at annual N inputs of about 270 kg N as mineral fertiliser and 100 kg N through excretion by grazing livestock. Although this is a small net emission flux it is significant due to the large area of the UK covered by grasslands (currently 65,574 km^2, Fuller *et al.,* 1994).

It remains a challenge to find an unequivocal explanation for the source and mechanism that causes the NH_3 emission after cut, prior to fertilization. Additional cuvette measurements by a GRAMINAE project partner (David *et al*., 2004), in-canopy concentration measurements at Braunschweig (Figure 5.30) and the PASIM model results suggest that two different mechanisms may contribute to this emission. The cuvette measurements and concentration profiles suggest that there is a ground level source in the mature canopy, probably from decomposing dead plant material. Normally, this NH_3 is recaptured by the canopy above and cannot escape the canopy. When this canopy this ground-level NH_3 is removed it is no longer recaptured and can easily be flushed out. The ecosystem model suggests a second, simultaneous process. After the cut CO_2 assimilation is reduced; indeed, net ecosystem respiration was observed for several days after the cuts at Easter Bush and Braunschweig. As a result, less of the N taken up by the plant is incorporated into the structural N pool and remains available in the symplastic and apoplastic pools thus increasing the stomatal compensation point.

For the first time, the role of fertilizer emissions for the formation of particulate matter has been quantified. At Braunschweig, particle growth rates of 400 nm hr^{-1} were observed above the canopy – larger than any growth rates observed in semi-natural environments. It is estimated that 0.13% of the fertilizer N applied was incorporated into airborne particles within 14 days of fertilization.

5.6.3. KEY DEVELOPMENTS IN PROCESS BASED MODELLING OF AMMONIA BI-DIRECTIONAL EXCHANGE.

Major advances have been made both in deriving generalised parameterisations of NH_3 exchange for application in atmospheric transport models and in linking NH_3 compensation points to ecosystem functioning.

Parameterisation of bi-directional ammonia exchange

As the bi-directionality of ammonia exchange is now widely accepted, suitable generalised parameterisations are now urgently required for incorporation into atmospheric transport models. Several of various complexity resistance routines exist (cf. Fig. 5.1), but the two-layer canopy compensation model of Nemitz *et al.* (2001b) is now recommended as the basis for generalisation (Fig. 5.26). The key parameters are the stomatal compensation point (Γ_s), which changes with N status and growth stage, the ground compensation point (Γ_g), which responds to management, the atmospheric resistances (R_a and R_b), which can be derived from meteorological parameters, the in-canopy resistances (R_{ac} and R_{bg}) which can be linked to canopy height and structure as well as turbulence, the stomatal resistance (R_s), which primarily responds to solar radiation and leaf area index and the cuticular uptake resistance (R_w), which is influenced by humidity, leaf surface chemistry and ammonia concentrations.

Significant progress has been made in prescribing parameterisations for UK grasslands. In particular, important, smooth parameterisations of Γ_s and Γ_g have been derived for the principal management activities (Fig. 5.28) for implementation in UK atmospheric transport models, while the evaluation of the measurements across the European transect continues to provide parameterisations for the range of European conditions.

Coupling ecosystem processes and NH_3 exchange

Up to now (non-dimensional) stomatal compensation points (Γ) have either been derived from micrometeorological flux measurements, from gas exchange measurements or from the NH_4^+ concentration and pH found in extractions of the leaf apoplasts. Through the incorporation of a NH_3 scheme into the ecosystem model PASIM the processes that regulate Γ are now beginning to be understood. In the current version of the model, plant cycling of NH_4^+ is described as the exchange between two pools of substrate N and one pool of structural N, which respond to N availability from the soil and atmosphere, C uptake and meteorological drivers. This model now sheds light on diurnal and seasonal cycles in Γ and its response to agricultural management. PASIM has been used to identify the origin of the post-cutting emissions (see above) and to explore management options. The scenarios suggest that NH_3 emission after fertilization may be reduced by 15 % if fertilization is delayed by two weeks as the recovered canopy is able to utilize the added N more readily. A current limitation for model scenarios is the need to prescribe air concentrations externally. As a next step, it is planned to integrate PASIM into a trajectory model, to allow for feedback between plant exchange and air concentration.

5.6.4. APPLICATION OF THE BI-DIRECTIONAL NH_3 EXCHANGE APPROACH FOR REGIONAL UPSCALING.

In addition to the implementation of the project results into the models described above, it is also of key interest to be able to use the results for national and European modelling of NH_3 transport and deposition. Work is now underway to utilize the compensation point modelling approach developed in a UK FRAME model of NH_3 dispersion, which estimates national deposition on a 5 km grid. At a European level, several meetings have taken place with the European Monitoring and Evaluation Programme (EMEP) of the Convention on Long-Range

Transboundary Air Pollution. Work has focused on agreeing a common SVAT structure for NH_3 and other pollutants, which would allow the model of Nemitz *et al.* (2001b) to be applied. This work is also being conducted collaboratively with the Stockholm Environment Institute at York, who is developing land cover/use maps which are necessary to implement the models. In particular, following these meetings, work is now underway at SEI with the aim to map 4 grassland types across Europe: grazed intensive grassland, grazed extensive grassland, cut intensive grassland (e.g. silage systems), cut extensive grasslands (e.g. hay systems), as well as separate maps of moorland/rough grazing land. These maps will provide an important input to allow the EMEP model to use the results from the UK grassland sites and the other sites along the GRAMINAE transect. The ongoing work will seek to obtain agreement on the parametrization of R_w as well as Γ for the different systems based on the results from the GRAMINAE sites. Given the nature of the EMEP model using a 50 km grid, farming activities are averaged and therefore, the time course of Γ as illustrated in Figure 5.28 will need to be smoothed in relation to regional growing seasons.

5.6.5. CONVENTION ON LONG RANGE TRANSBOUNDARY AIR POLLUTION

The UNECE Convention on LRTAP represents one of the key users of the project results through a number of its working groups. In particular, CEH has been active in feeding results to the Ammonia Expert Group, the Task Force on Measurement and Modelling and the European Monitoring and Evaluation Programme.

UNECE Ammonia Expert Group

The Ammonia Expert Group reports directly to the Working Group on Strategies and Review of the Convention and has been tasked specifically with assessing the potential to abate NH_3 emissions in the UNECE region and on reporting on the uncertainties in abatement methods. For example, the group provided the annex on ammonia abatement included in the 1999 Gothenburg Protocol.

Although there is a wide range of established NH_3 abatement methods, there has been significant doubt regarding their effectiveness in practice. This was highlighted by the observation by GRAMINAE scientists that NH_3 concentrations in the Netherlands did not decrease as expected following implementation of a national NH_3 abatement policy (Erisman and Monteny 1998). This discrepancy has become know as the "Ammonia Gap". Further uncertainties were identified, when it was noted that although animal numbers decreased substantially in Eastern Europe after 1989, there was no apparent reduction in either NH_3 or NH_4^+ from monitoring in Hungary (Horváth and Sutton 1998). CEH work supported by the Acid Deposition Processes project contributed to the analysis of this problem through reviewing the literature on European NH_3 and NH_4^+ trends (Sutton *et al.* 2001c) as background for the AEG Working Groups, which have been reported by Menzi and Acherman (2001) and to the UNECE (2001).

At the recent meeting of the AEG in Bologna (November 2001), a concerted effort was placed to revise the Technical Annex on ammonia of the Gothenburg Protocol. CEH staff were closely involved in this process, ensuring that relevant results of the project are fed into the revision. Two examples of recommendations for the Protocol Annex are given in Box 1, in relation to NH_3 emissions from fertilizers and measures to reduce NH_3 emission by grazing management.

***EMEP: Modelling ammonia fluxes at a European Scale*.**

As noted above, work to apply the results of GRAMINAE in European pollutant transport modelling is now ongoing with staff of the European Monitoring and Evaluation Programme (EMEP) of the Convention. Meetings have sought to agree on the basic structure of the model resistance framework, parameterisation of resistance terms and Γ values, as well as establish land use/land cover databases that allow application of the models. This work is not just relevant for NH_3, but is being conducted in parallel with treatment for ozone and other pollutants in collaboration with the Finnish Meteorological Institute, the Stockholm Environment Institute at York and the University of Bradford.

UNECE Task force on Measurement and Modelling

The UNECE Task Force on Measurement and Modelling provides the interface to link EMEP with national experts in the field of dispersion and deposition modelling for the Convention. Within this framework, the GRAMINAE coordinator has reported the findings of the UNECE Ammonia Expert Group, highlighting the needs to develop methods to monitor compliance of NH_3 emission abatement methods. A key issue has been the need to implement monitoring of NH_3 and NH_4^+ across Europe, as for many countries this is too expensive. Bearing these constraints in mind, a low-cost denuder sampling method (Sutton *et al.* 2001d) has been presented with a view to encouraging wider monitoring of NH_3 and NH_4^+ across Europe.

5.7. Project outputs

Refereed Journals

In preparation or under review

Dynamics of ammonia exchange with cut grassland: objectives and measurement strategy of the GRAMINAE integrated experiment. (Sutton, Nemitz, Schjoerring, Mattsson, Hensen, Cellier, Loubet, Roche, Neftel, Horvath, Weidinger, Rajkai, Theobald, Gallagher, Burkhardt, Daemmgen)

Inter-comparison of measurements and assessment of the turbulent exchange and energy balance of an intensively managed grassland (K.J. Hargreaves, E. Nemitz, A. Neftel, B. Loubet, P. Cellier, J. Dorsey, M. Flynn, A. Hensen, T. Weidinger, R. Meszaros, L. Horvath, C. Fruehauf, M.A. Sutton, M. Gallagher)

Ammonia fluxes in relation to cutting and fertilization of intenstively managed grassland derived from an inter-comparison of gradient measurements (Milford C., Theobald M.R., Nemitz E.N., Hargreaves K.J., Horvath L., Raso J., Daemmgen U., Monica, Neftel A., Jones S., Hensen A., Loubet B., Sutton M.A.)

Turbulent statistics and transport mechanisms within grass canopies. (Nemitz E., Loubet B., Cellier P., Lehman B., Neftel A., Hargreaves K.J., Theobald M.R. and Sutton M.A).

Parametrization of NH_3 exchange with an intensively managed grassland using a canopy compensation point resistance model (Sutton M.A., Milford C., Mosquera J., Nemitz E., Theobald M.R., Hargreaves K.J., Erisman J.W., Herrmann B., Horvath L., Borella S., Neftel A., Mattsson M.E., Schjoerring J.K, T. Weidinger and J. Burkhardt)

Application of a coupled grassland – gas exchange model to investigate the interactions between grassland management and NH_3 fluxes. (M. Riedo, C. Milford, M.E. Mattsson, J.K. Schjoerring, B. Herrmann, K. Fruehauf, M. David and M.A. Sutton),

Gas-to-particle conversion above grassland, following the application of NH_4NO_3 fertilisers (Nemitz E., McFiggins G., Dorsey J., Gallagher M.W., Erisman J.W., Otjes R.P., Jongejan, P. and Sutton M.A.).

Dynamics of ammonia exchange with cut grassland: synthesis of results and conclusions (M.A. Sutton, C. Milford, E. Nemitz, J.W. Erisman, A. Hensen, P. Cellier, M. David, J.K. Schjoerring, M.E. Mattsson, J. Dorsey, M. Gallagher, L. Horvath, M. Riedo, U. Daemmgen, A. Neftel, B. Herrmann, B. Lehman and J. Burkhardt)

Nemitz E., Sutton M.A., Wyers G.P. and Jongejan P.A.C.: Gas-particle conversions above a Dutch heathland: I. Surface exchange fluxes of NH_3, SO_2, HNO_3 and HCl. *Atmos. Chem. Phys.* [under review]

Nemitz E., Sutton M.A., Wyers G.P., Otjes R.P., Mennen M.G., van Putten E.M., Hellemond J. and Gallagher M.W.: Gas-particle conversions above a Dutch heathland: II. Concentrations and surface exchange fluxes of atmospheric aerosol particles. *Atmos. Chem. Phys.* [under review]

Nemitz E. and Sutton M.A.: Gas-particle conversions above a Dutch heathland: III. Modelling of size-dependent NH_4^+ fluxes as modified by the NH_3-HNO_3-NH_4NO_3 equilibrium. *Atmos. Chem. Phys.* [under review]

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Acid Deposition Processes:
Cloud composition monitoring.

EPG 1/3/166

Neil Cape, David Fowler, Frank Harvey, Alan Crossley, Karl Beswick and Tom Choularton

Centre for Ecology and Hydrology
(Edinburgh Research Station)
Bush Estate, Penicuik,
Midlothian, EH26 0QB, UK.

Department of Physics
UMIST
PO Box 88
Manchester, M60 1QD,UK

Cloud and rain composition monitoring

- Cloud and rain composition measurements at Dunslair Heights show long-term trends downwards in nitrate and non-sea sulphate concentrations, but relatively small changes in recent years.
- There have been large changes over time in the proportion of precipitation sampled as cloud water at Dunslair, most probably caused by the growth of the nearby forest.
- Potential interference by trees has meant that the site has been moved to a similar elevation a few km to the north.
- Cloud and rainfall amounts have increased since 1991 at Holme Moss.
- Concentrations of both nitrate and non-sea sulphate have decreased at Holme Moss in both cloud and rain over the past 5 years.
- There is evidence of source limitation for nitrate deposition at high rainfall (i.e. concentrations decline at the largest rainfall amounts).
- A paper summarising all the results to 2001 has been published (K M Beswick, T W Choularton, D W F Inglis, A J Dore and D Fowler (2003) Influences on long-term trends in ion concentration and deposition at Holme Moss, Atmospheric Environment, Vol 37, pp 1927-1940.)

6. MONITORING OF CLOUD AND RAIN CHEMISTRY AT HIGH ELEVATION.

6.1. Dunslair Heights

Weekly sampling of cloud, using a lidded cloud collector, and adjacent bulk precipitation has continued at the summit of Dunslair Heights, near Peebles, to provide a long-term dataset, which started in 1987. An additional bulk precipitation sample is taken at a lower elevation (Venlaw) on the same hill, for comparison.

6.1.1. TEMPORAL TRENDS

Trends in concentrations of major ions up to 2002 are shown in Figure 6.1.

Nitrate concentrations have remained almost constant since 1998 in precipitation at both upper and lower sites, at around 15 µM, substantially less than at the end of the 1980s, when the concentrations were twice as large. A similar decrease in concentration has been seen for the cloud samples, although volume-weighted average concentrations are much larger, at around 100 µM, compared with 250 µM in the late 1980s. The ratio of concentrations in cloud relative to rain has been variable between 5 and 12 over the period, with no clear time trend (Figure 6.2).

Non-marine sulphate concentrations in both rain and cloud have also changed little over the past 5 years, with current average concentrations in rain around 10 µM (20 µeq l^{-1}), and around 60 µM (120 µeq l^{-1}) in cloud. The ratio of concentrations in cloud relative to rain has shown a small upward trend with time, from around 5 in the late 1980s, to around 7 in the 2000s (Figure 6.2).

Ammonium concentrations have shown little consistent trend at the lower elevation site, where concentrations are larger than at the summit, and where there may be local sources of ammonia nearby. At the summit there has been a small but continual decrease in annual average concentrations with time since the mid 1990s, and this pattern is also seen in cloud concentrations. Annual bulk rainfall concentrations at the summit are now around 15 μM, compared with around 100 μM in cloud.

The contribution of sea-salts to the composition of rain and cloud is shown in terms of the sodium ion concentrations in Figure 6.3. Apart from a very large annual average in 1989, concentrations have not varied much from year to year in either cloud or rain, but there has been a gradual but persistent decrease in concentrations in rain from the mid 1990s, and an increase in concentrations in cloud over the same period. This has led to a marked increase in the ratio of sodium in cloud relative to sodium in rain, from a minimum of around 7 in the early 1990s to the current value of 25 (Figure 6.2).

6.1.2 INTERPRETATION AND DISCUSSION

Although the decreases in concentrations of nitrate and non-marine sulphate over time are broadly in line with the pattern of emissions of NOx and SO_2 in the U.K., there has been concern that the growth of trees close to the sampling site at the summit of Dunslair Heights has interfered with the sampling of cloud water. The clearest evidence for this is shown in Figure D, which plots the amounts of water sampled by the cloud gauge and the two bulk rain collectors, expressed as a precipitation depth. It is clear that the amount of cloud water collected by the sampler is very much less now, relative to amounts of precipitation, than it was during the period up to the mid 1990s. In the absence of any evidence that the frequency or duration of cloud cover has changed in the region, and the obvious growth of the forest adjacent to the sampling site at Dunslair, it appears that the site is being compromised for long-term monitoring by the growth of the trees.

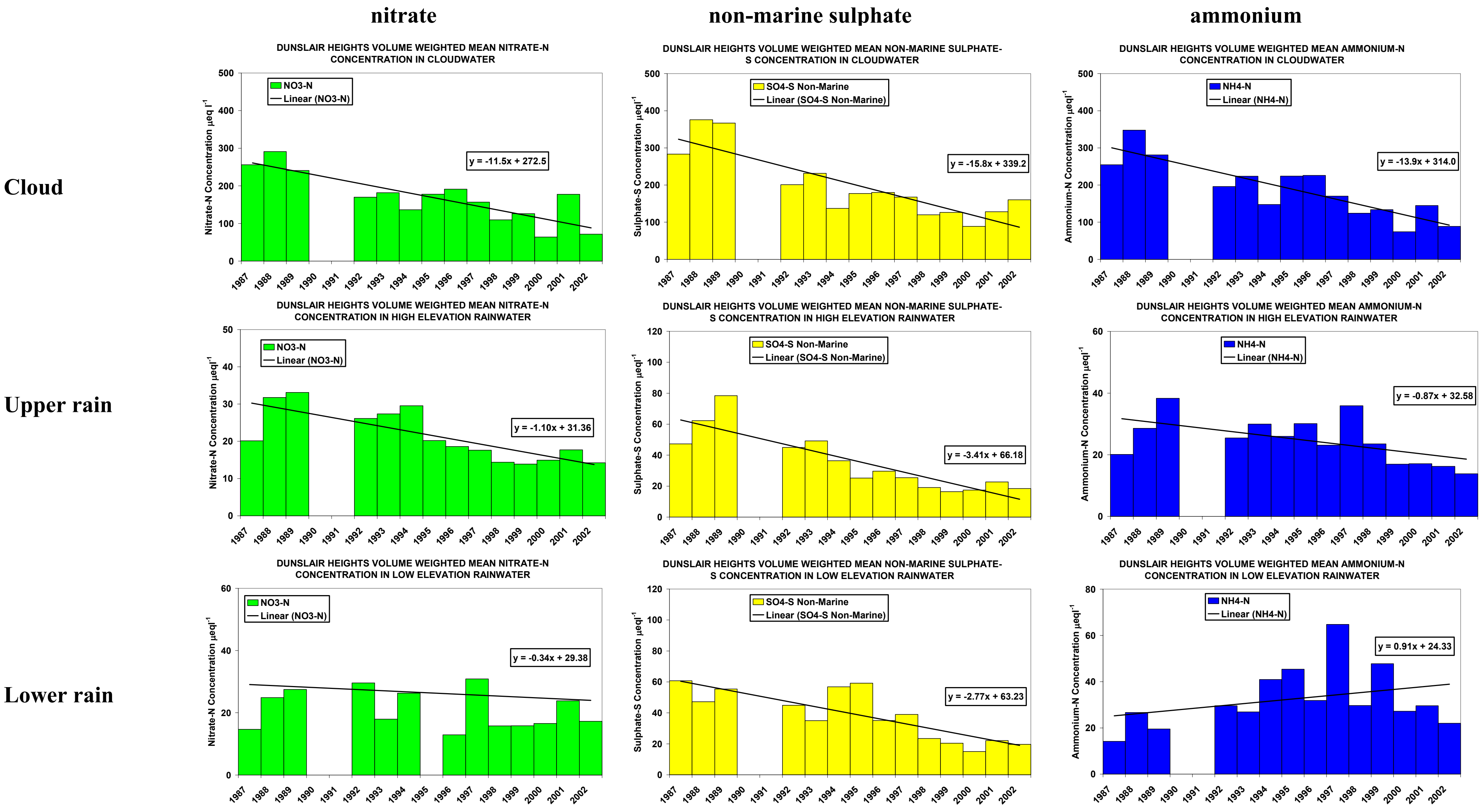
The decrease in amounts of cloud water sampled may also be partly responsible for the change in the ratio of sodium concentrations between cloud and rain. Smaller cloud capture rates may be caused by a systematic reduction in the size of droplet sampled by the collector, either because average cloud base is higher (droplet size increases upwards in a cloud from the cloud base), or because larger droplets are increasingly intercepted by the surrounding forest. Smaller droplets are likely to have larger concentrations than large droplets. However, this hypothesis is not borne out by the relative stability over time of the concentration ratios between cloud and rain of nitrate and non-marine sulphate. There may be more subtle interactions with the surrounding forest, influencing the pattern of wind direction at the site. High sodium (sea-salt) concentrations are usually seen in south-westerly air flow, whereas the largest nitrate and non-marine sulphate concentrations are observed in easterly and south-easterly flow.

For these reasons, and because of doubts over the long-term future of the site at Dunslair Heights, it has been decided to move the samplers to Bowbeat Hill, a hill of similar elevation, approximately 3 km north of Dunslair Heights, but with no trees. Although this means a change in the sampling location, it is clear that the continued use of Dunslair Heights cannot be justified, given the potential effects of the growing forest on air flow patterns over the hill. Relocation to Bowbeat will permit us to decide whether the change in cloud water amounts observed at Dunslair Heights have been caused by a systematic change in the frequency and duration of cloud events, possibly related to climatic change, or whether the observations are simply an effect of the growth of the forest.

6.1.3 DESCRIPTION OF THE NEW MONITORING SITE AT BOWBEAT

The Bowbeat site has been constructed for the collection of rain and cloud water for ion chemistry, heavy metals and bacteria in cloud water. It is located at UK Grid reference NT283473 (N55:42:51 W3:08:35),(see Figure 6.5). This is just 3.5 km north of the existing Dunslair Heights monitoring site and is in an area of open moorland, 580 metres a.s.l., adjacent to the Bowbeat wind farm complex (Figures 6.6, 6.7). The collecting equipment is enclosed by a 25m x 25m fence and is located on the SW side of a gentle knoll called Bowbeat Rig. The 24 Turbines are 46 metres to the hub with 60 metre diameter rotors and form the largest operational wind farm in Scotland. The nearest unit is 200m away from the monitoring site. The 60m meteorological mast is part of the wind farm operation but could provide a potential source of power and instrument location.

Figure 6.1. **Trends in concentrations 1987-2002 (μeq l^{-1})**



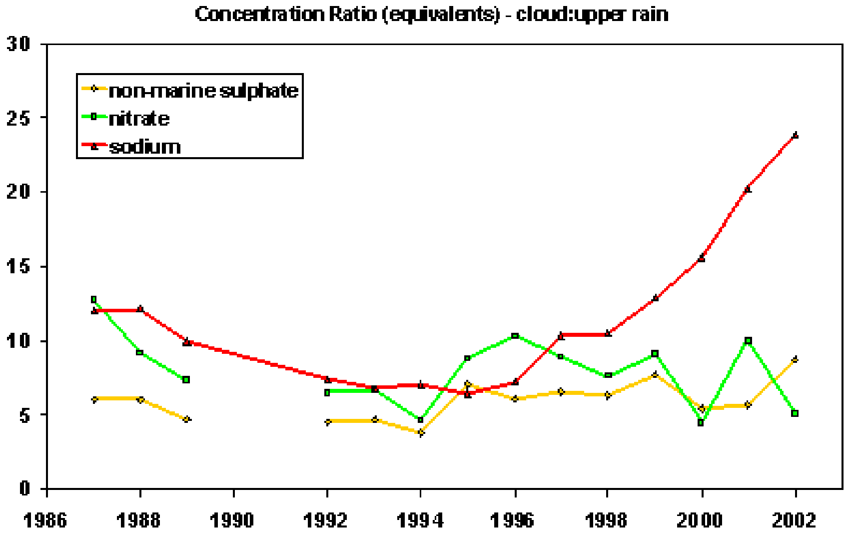


Figure 6.2. Ratio of concentrations of ions in cloud and rain at Dunslair Heights between 1987 and 2002

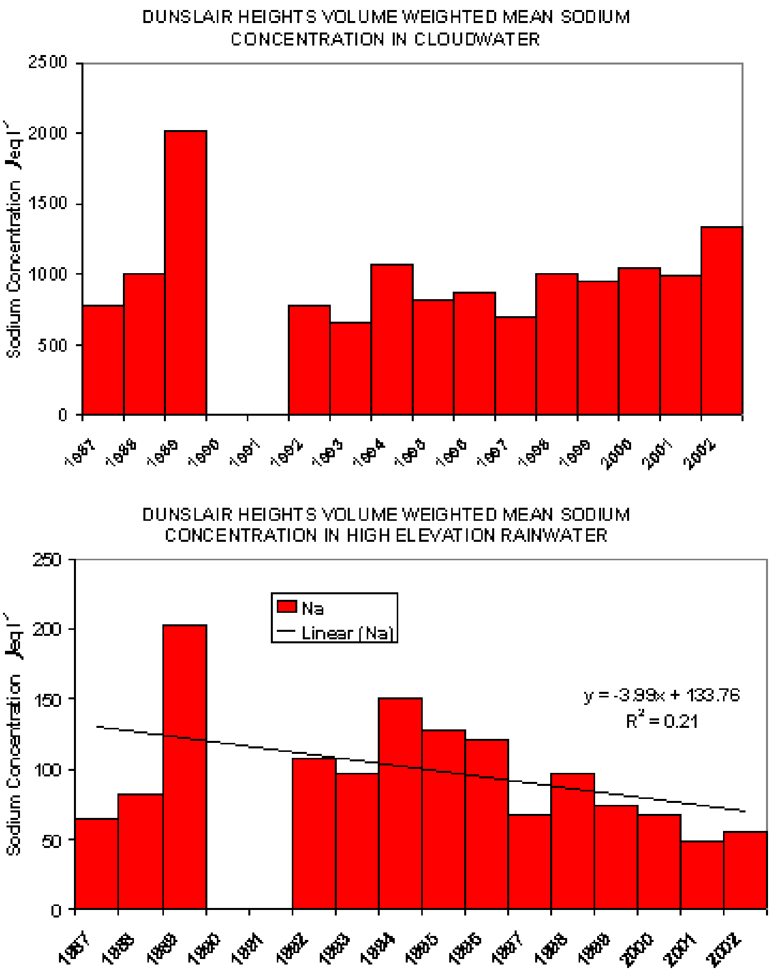


Figure 6.3. Sodium concentrations in cloud (upper chart) and rain (lower chart) at Dunslair Heights, between 1987 and 2002

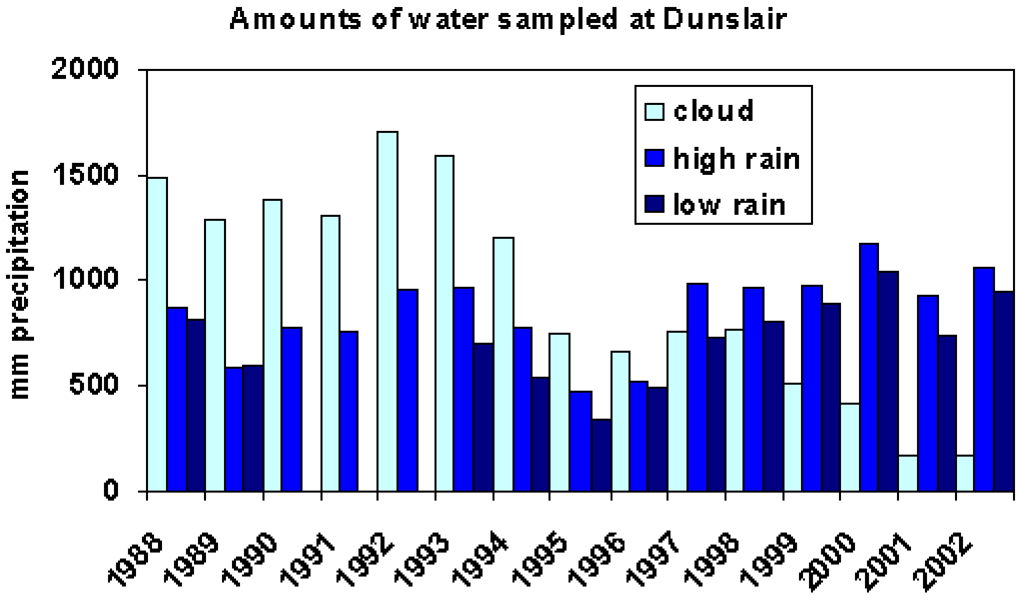


Figure 6.4. Amounts of water sampled by the cloud collector and both bulk precipitation collectors (summit and lower slope) at Dunslair Heights, between 1987 and 2002

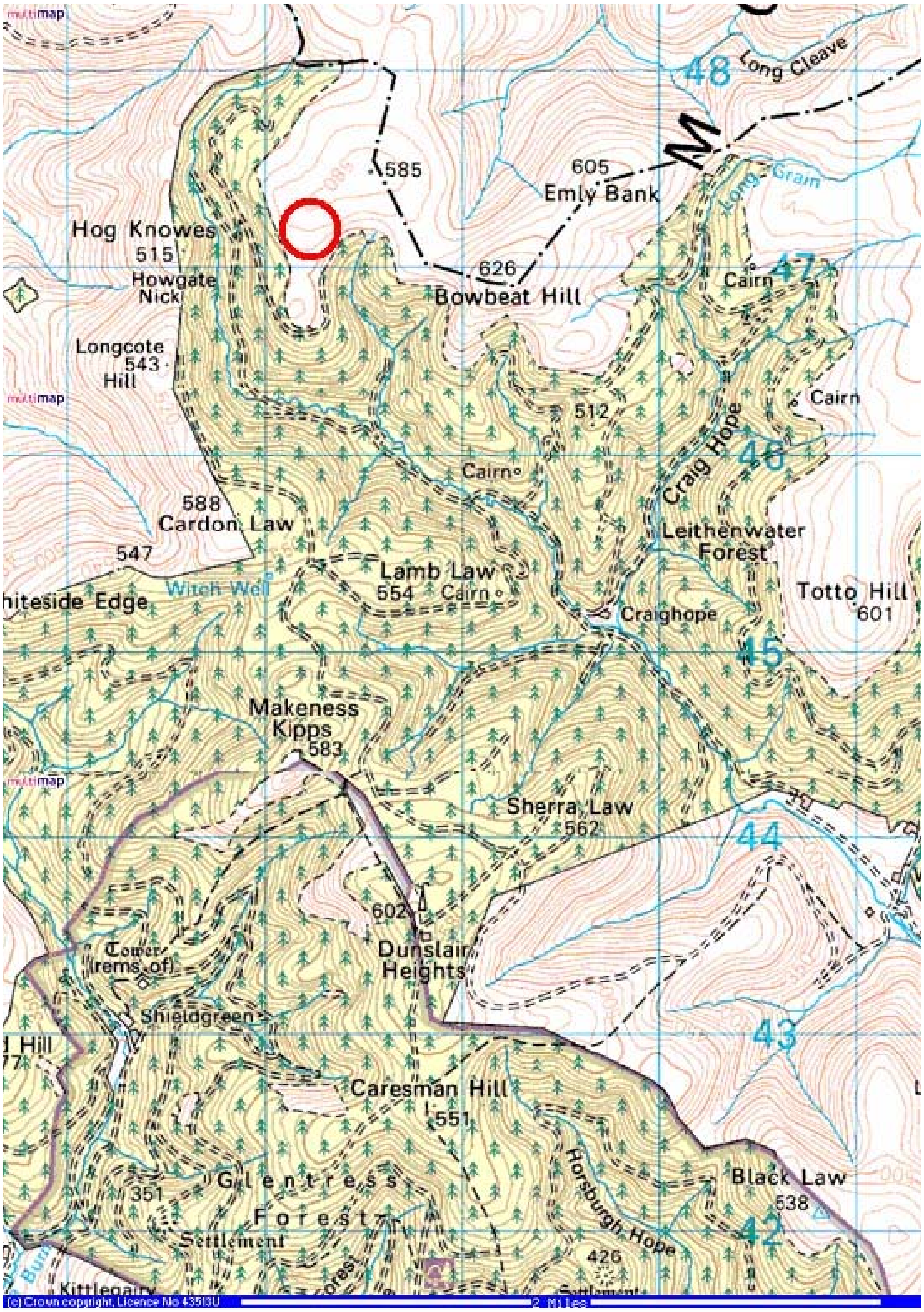


Figure 6.5. Map showing location of new Bowbeat site in relation to Dunslair Heights.

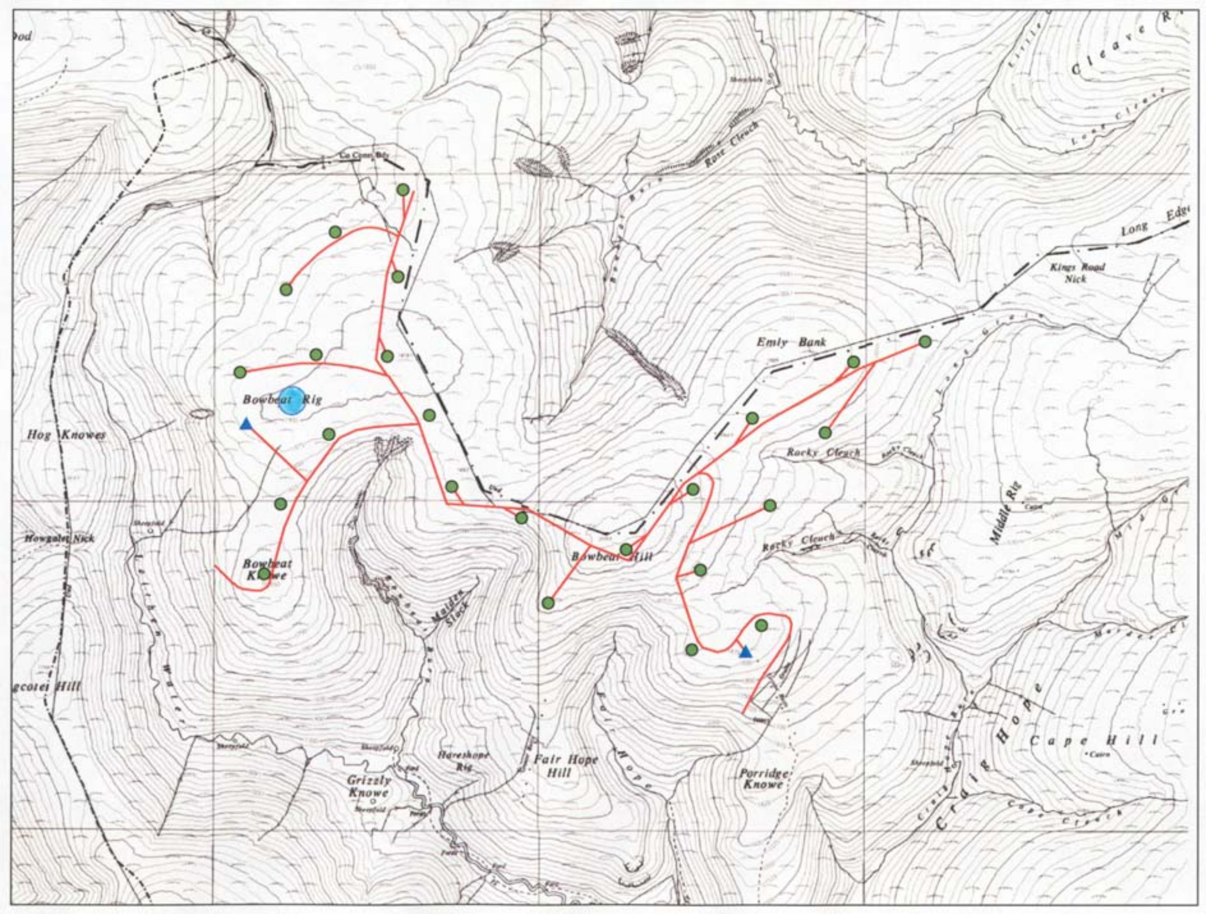


Figure 6.6. Detailed map The location of the CEH cloud samplers is shown as a blue circle.showing location of wind turbines at Bowbeat Hill.

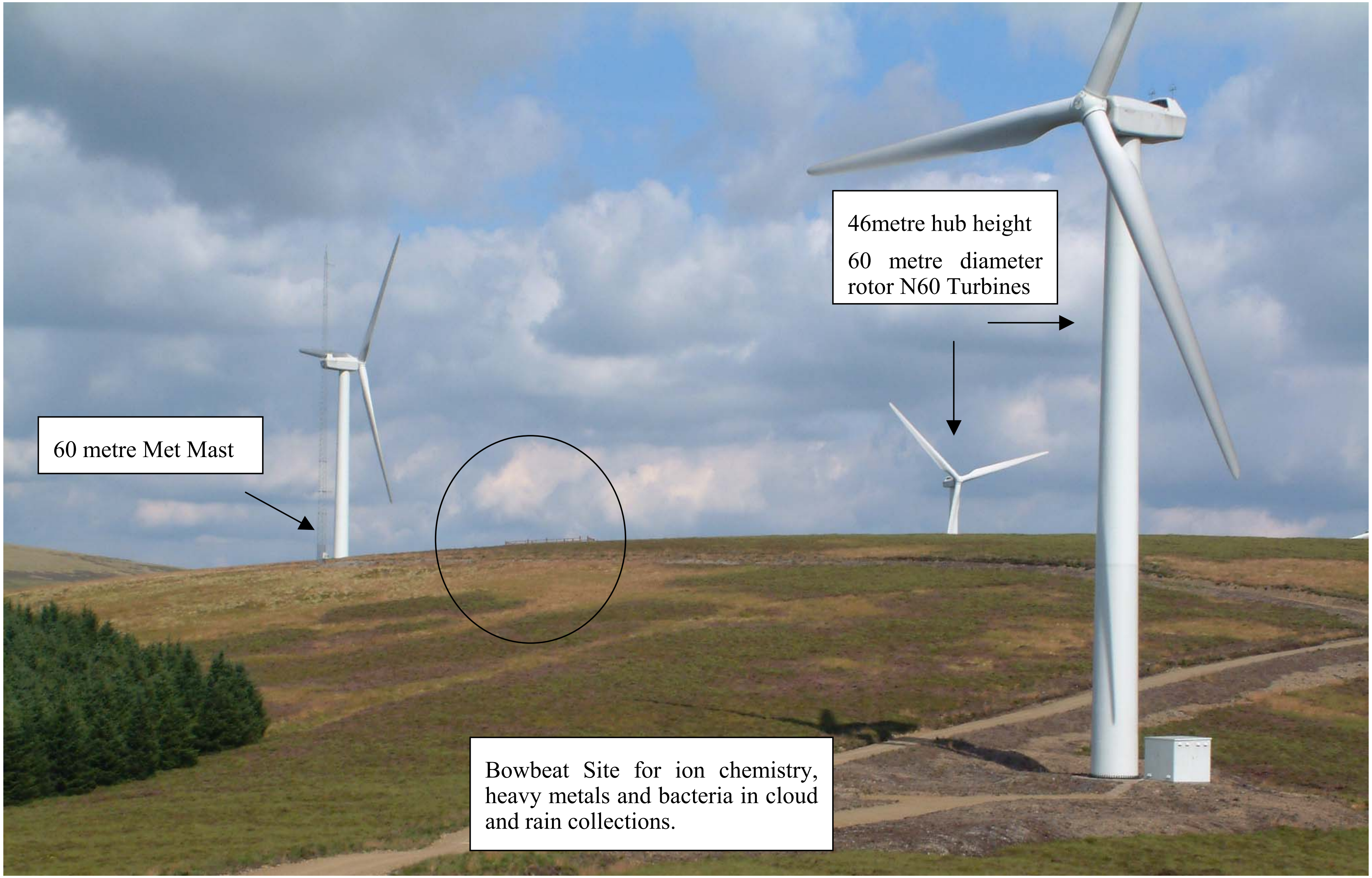


Figure 6.7. Location of new Bowbeat site in relation to wind turbine

6.2. Summary of Holme Moss Activities, January 2001 to August 2003

6.2.1. INTRODUCTION

Work at Holme Moss continues to progress, with upgrades in computational and logging facilities, the preparation and publication of papers, and the presentation of data at conference. Instrumentation at the site remains reliable, with one exception.

6.2.2. EQUIPMENT

Automatic Weather Station

The AWS has provided reliable data throughout most of the period. There were multiple sensor failures during Mar-June 2001, and a logger failure in June 2002. Long-running problems with the back-up tipping bucket raingauge have been resolved, although the main raingauge appears to be adversely affected by high wind speeds (in excess of 15 m s^{-1}). The cloud collector attached to the tipping bucket raingauge has been removed pending use on a project being run by the University of East London (see below).

Present Weather Sensor

The PWS continued to provide almost 100% data coverage until being struck by lightning in late October 2002. Extensive damage was sustained by most of the electronics, resulting in a lengthy repair time. However, on redeploying the sensor in February 2003, it was again struck by lightning within a week, causing further extensive damage. Subsequent repairs involved upgrading of the electronics, with the unfortunate side-effect of rendering the instrument susceptible to RF interference. Since the Holme Moss site is home to a major TV/radio broadcasting mast, this posed a serious problem, with the instrument now incapable of accurately reporting the precipitation state. A number of visits to BIRAL have failed to cure this problem. A much newer probe is currently on loan from BIRAL in order to help determine which part of the older probe is now subject to RF interference. The loan probe is currently functioning perfectly.

An AVM, which is an older version of the PWS, was installed on site during March 2003. This probe was originally designed to be mounted on an aircraft. The main output parameters are extinction coefficient, precipitation type and cloud intensity. This instrument is proving to be reliable, with the extinction coefficient correlating linearly with that given by the PWS.

Bulk Collectors

The bulk collectors are still functioning reliably. The cloud collector will need to be restrung in the near future, with part of the collector assembly requiring replacement (which has been provided by CEH). It may also be desirable to replace the downpipes from the collecting funnel to the collecting containers. Bulk samples continue to be taken weekly every Thursday. The weekly visit also enables site maintenance to be carried out.

The Cabin

The cabin will require some remedial work during the next year, since some of the weatherproofing has started to fail. In places this has resulted in patches of rotten wood which will require replacement. It is also evident that over the years, the cabin has “settled” and is no longer horizontal. It is therefore desirable that the cabin be re-levelled at some point, particularly if it is to be used for other projects.

6.2.3. COMPUTING AND DATA ANALYSIS

Computing

Computing facilities at the site were upgraded in October 2002. A Windows 2000 system equipped with a multi-serial card now logs the AWS, PWS and AVM. The AWS is controlled by the latest version of Campbell’s LoggerNet, whilst the other instruments ae logged using LabView. The serial card allows for up to five other instruments to be logged if necessary. The new computer logs in to the UMIST network once a day: a desktop computer at UMIST can then directly access the logging computer in order to back-up the AWS and PWS data. It will shortly be possible to dial up the logging computer from UMIST at any time.

Ion Analysis

Chemical analysis of the bulk samples continues to be carried out at UMIST. At present, analyses are available up to the end of September 2002, with delays in processing caused by the demands of other projects.

Data Processing

Most of the processed data from the AWS, PWS, AVM and chemical analysis are available in the form of Excel spreadsheets. The extensive network of files is designed to allow easy updating of annual averages, direction dependence of ionic concentration and deposition, and instrument comparisons. This also enables problems with data to be spotted at the earliest opportunity.

6.2.4. PUBLICATIONS

A paper (Beswick *et al.* 2003) covering Holme Moss data from 1994-2001 was submitted in August 2002 and published in January 2003 in Atmospheric Environment. This paper focussed on the long-term trends in ion concentration and deposition at Holme Moss in relation to national trends, source location and reduction in emissions over the last decade. The main points from this paper are outlined below.

A second paper is currently being prepared, reviewing wet deposition research in the United Kingdom. This will be mainly an overview of seeder-feeder enhancement work and it’s impact on wet deposition modelling. Datasets covered will include Holme Moss, Great Dun Fell, Winter Hill, Saddleworth Moor, Snowdonia, Dunslair Heights and a number of other smaller studies.

The data covered by the Atmospheric Environment paper was presented orally at the Royal Meteorological Conference in Norwich in September 2003.

Other work

At the request of the University of East London, one of the cloud collectors at Holme Moss has been prepared for use in a project to collect cloudwater. The premise of this project is that material of biological origin can act as cloud condensation nuclei. To this end, a sample of cloud water is required which is free from any biological contamination, specifically DNA. The cloud collector has required extensive preparation, and is currently at UEL awaiting fresh preparation following an aborted attempt to collect a sample.

During June and July 2001, in response to a request from the University of Lancaster, a passive sampler collecting Persistent Organic Compounds was deployed at Holme Moss, along with a second collector on the roof of the Pariser Building at UMIST.

6.2.5. TRENDS IN ION DEPOSITION AND CONCENTRATION AT HOLME MOSS

The current state of annual-averaged data available from Holme Moss has not progressed significantly over that presented in Beswick *et al.* (2003) which covers the years 1994-2001. Whilst all AWS and PWS data have been prepared, all rain and water samples from September 2002 onwards are still awaiting IC analysis.

A full update on trend analysis must wait until the 2002 data are available, and preferably would also encompass the 2003 results. The 2003 data are expected to add significantly to the data set since up to August 2003 it has been the driest year at Holme Moss since 1997, experiencing only 55% of the 2002 rain total. In the paper, scavenged cloud water data was not available for 2001 because of a lack of data from the low-level comparison site at Wardlow Hay Cop. Data from this site are now available for 2001 and 2002, but only in provisional form.

Beswick *et al.* (2003) report results both as time histories and also relative to rain and cloud amount. For data up to 2001, there was a clear upward trend in annual rainfall and cloud amount. Deposition of the major ions was dominated by the increase in rainfall, with deposition increasing despite decreases in ionic strength. The decreasing concentration was thought to be principally due to the action of the seeder-feeder process. For the wetter years, the spatial and temporal extent of the cap cloud was expected to be greater than for the drier years. This allows more time for rainfall volume enhancement, but also implies deeper clouds with, on average, larger cloud droplet sizes. Since larger droplets have in general a lower ionic strength than smaller droplets, the seeder rain scavenges more dilute water from the cloud, leading to a reduction in ionic enhancement. Conversely, in drier years such as 1995, the presence of cap clouds at Holme Moss is much reduced, with correspondingly shallower clouds with more concentrated smaller cloud droplets. This results in smaller volume enhancement for rain, but higher concentration in scavenged cloud water and cloud sampled at Holme Moss.

Whilst deposition of nss-sulphate, sodium and chloride continued to increase with rainfall amount, deposition of nitrate was seen to tail off at high annual rainfall. This was due to a source-limiting effect. Two factors were thought to come into play: enhanced washout of aerosol upwind of Holme Moss; insufficient time for pollution emitted in the Manchester/Liverpool conurbation to be fully processed into aerosol before arrival at the site.

Whilst much of the reduction in rain and cloud ionic strength was attributed to the seeder-feeder process, some was also thought to be a response to reductions in sulphur and nitrogen emissions brought about through emissions control protocols. This was inferred by comparing the rate of change of concentration of the marine ions sodium and chloride with that of the mainly anthropogenically sourced non-sea-salt-sulphate and nitrate ions. The marine ions declined in concentration proportionally slower in concentration on average over the period 1994-2001 than did the anthropogenic ions, with concentration of sodium in rain falling by 16%, whilst nss-sulphate and nitrate concentrations declined by 42% and 25% respectively. For scavenged cloud concentration, sodium, nss-sulphate and nitrate declined by 28%, 44% and 39% respectively.

On a UK wide scale it is apparent that a marked decline in sulphur dioxide emissions has occurred, however decreases in wet deposited sulphate have only been noted in the regions of the UK close to emission sources. A number of possible explanations for this have been offered, however, work has proceeded to investigate the role of oxidants in this process. Hydrogen peroxide is the only rapid oxidant in the aqueous phase, which acts independently of pH, however this reaction is severely oxidant limited in polluted regions. The other oxidant ozone is abundant but requires a cloudwater pH above about 4.2. This requires that the sulphuric acid produced by oxidation of aqueous SO_2 is neutralised by ammonia. It is clear, therefore, that the rate of SO_2 oxidation will be controlled by ammonia gas in polluted regions. Hence one would expect a linearity between emissions of sulphur dioxide and sulphate deposition in rain to occur in regions with high ammonia concentrations. Evidence for this can be found in the Holme Moss data (see Figure 6.8). This argument is presented and discussed in Choularton and Bower (2001).

Although the full ion analysis is not available for 2002, monthly averages of rain and cloud concentrations of nitrate and nss-sulphate are shown in Figures 6.9 and 6.10.

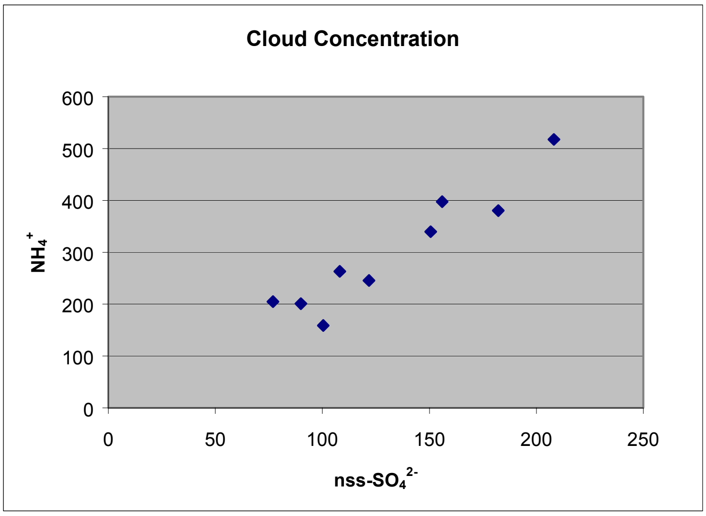


Figure 6.8. Relationship between ammonium and nss-sulphate concentrations at Holme Moss

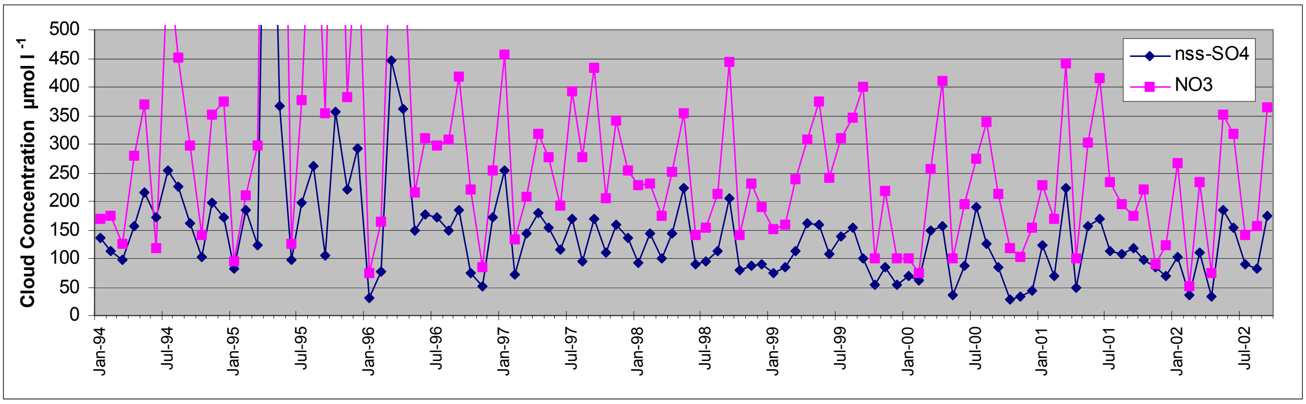


Figure 6.9. Concentration of nitrate and sulphate in cloud at Holme Moss

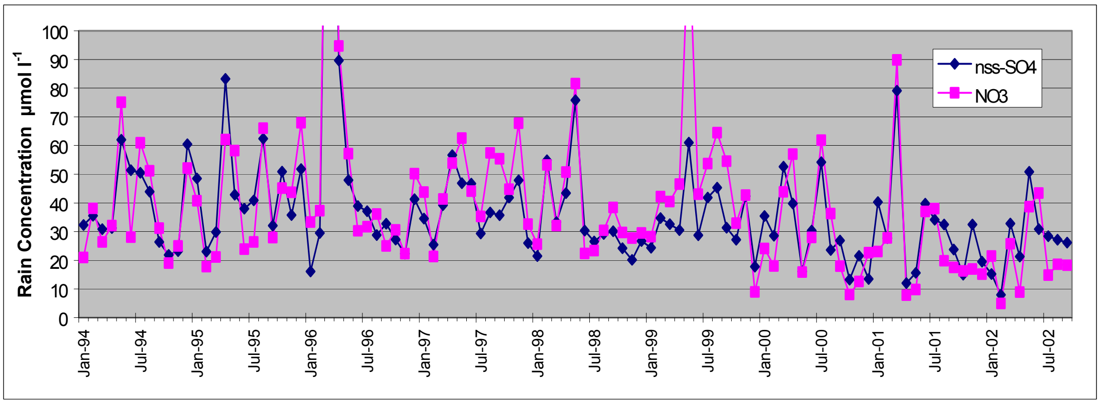


Figure 6.10. Concentration of nitrate and sulphate in rainwater at Holme Moss

Acid Deposition Processes:
Total deposition and Trends.

EPG 1/3/166

D. Fowler

Centre for Ecology and Hydrology
(Edinburgh Research Station)
Bush Estate, Penicuik,
Midlothian, EH26 0QB, UK.

Total Deposition of Sulphur, Nitrogen Acidity and Base cations and Trends

- Deposition of non-marine sulphur in the UK has declined from 600kt in 1987 to 190 kt in 2001, a reduction of approximately 70%, during a period in which emissions declined from 1966 kt S to 480 kt S.
- Trends in deposition of oxidized nitrogen are uncertain due to the short period of HNO_3 monitoring. However, trends in precipitation NO_3^- are small, and only statistically significant in the English Midlands. Over the UK, the wet deposition of oxidized N has remained fairly constant at about 100 kt N, dry deposition of NO_2 has declined from about 60 to 30 kt N and the deposition of HNO_3, which is currently about 60 kt N is unknown earlier than 2000.
- Trends in the dry deposition of reduced N appear to have declined by about 10% over the period 1996 to 2000 and wet deposition has declined by about 10% between 1986 and 2001. Overall there does therefore appear to be a small reduction in reduced N deposition over a period in which emissions have declined by about 10%.
- Deposition of non-marine chloride has declined by about 80% between 1986 and 2001, but the absolute values are subject to substantial uncertainty due to analytical problems.
- Base cation wet deposition in the UK declined between 1986 and 2001 by between 30% and 40% and is subject to substantial uncertainty. Dry deposition is uncertain but probably declined by a similar magnitude.

7. TOTAL DEPOSITION AND TRENDS

The total deposition of Sulphur, oxidized and reduced Nitrogen compounds to the UK have changed in response to changes in emissions, as shown in Table 7.1.-7.3. below. The reduction in Sulphur deposition is a notable policy achievement for the UK and the monitoring networks and assessment show the trends throughout the UK. The reductions in Nitrogen deposition are much smaller and, in part due to smaller reductions in emissions, especially of reduced Nitrogen, but there is clear evidence of the non-linearities observed earlier for Sulphur (NEGTAP 2001). The cause of the very small reduction in oxidized Nitrogen deposition following a reduction in emissions of approximately 45%, remain unknown. However, there are two strong candidates, the contribution to UK deposition from increases in marine emissions during the last two decades, especially in the eastern Atlantic. Second, there is evidence that the average transport distance for oxidized nitrogen has declined, resulting in a larger fraction of UK emissions being deposited within the UK, and a smaller export. The new aerosol and HNO_3 measurements are very helpful in closing the UK budget from the measurements. However, these are recent and do not help to define the position in the mid 1980s. There are therefore very important aspects of the Nitrogen budget that remain to be defined in order to show the response to past changes in emissions and to forecast the effects of current strategies.

In addition to the changes in emissions and atmospheric chemistry, it is important to note the changes in the processes of measurement and modelling deposition. During this contract the UK deposition budget for Nitrogen has changed due to the addition of HNO_3 to the concentration and deposition field, the deposition of NH_3 has changed following changes to the deposition modelling procedures. Lastly the aerosol deposition of both Sulphur and Nitrogen compounds has now been quantified, following the development of a UK network of aerosol samplers for the regional background concentration field. The deposition of aerosols contributes an additional 17 kT S, 13kT oxidized N and 11 kT reduced N, and are therefore small parts of the budget. However, the additional aerosol deposition will influence the exceedance maps when the new total deposition maps are used for the assessment of environmental effects using Critical Loads methods.

Table 7.1. UK sulphur budget from the network measurements 1986-2001 (kt S

Year	Emissions	Wet deposition	Dry deposition	Total deposition
1986	1939	252	415	667
1987	1937	238	290	528
1988	1905	242	234	476
1989	1848	199	223	422
1990	1860	194	199	392
1991	1768	196	232	428
1992	1731	222	189	411
1993	1558	192	168	360
1994	1338	206	156	362
1995	1183	164	146	310
1996	1015	183	145	327
1997	835	148	111	258
1998	804	162	94	256
1999	615	149	82	231
2000	594	138	73	212
2001	563	133	76	209

Table 7.2. UK Oxidised nitrogen budget from network measurements 1986-2001 (kt N)

Year	Emissions	Wet deposition	Dry deposition	Total deposition
1986	797	106		106
1987	831	112		112
1988	848	111		111
1989	848	101		101
1990	841	90		90
1991	803	103		103
1992	779	109		109
1993	719	105		105
1994	689	126		126
1995	635	101		101
1996	613	104	27	131
1997	561	102	37	139
1998	527	98	33	132
1999	488	103	31	135
2000	460	98	89	187
2001	511	105	101	206

Table 7.2. UK Reduced nitrogen budget from network measurements 1986-2001 (kt N)

Year	Emissions	Wet deposition	Dry deposition	Total deposition
1986		135		135
1987		129		129
1988		119		119
1989		125		125
1990	294	119		119
1991	296	132		132
1992	285	131		131
1993	285	109		109
1994	287	136		136
1995	279	120		120
1996	281	135	71	206
1997	286	116		116
1998	280	121		121
1999	280	121	53	174
2000	266	104		104
2001	261	120		120

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ANNEX

A detailed Desciption of Wet, Cloud and Dry Deposition

Wet deposition

MONITORING AND MAPPING CONCENTRATION OF IONS IN PRECIPITATION AND PRECIPITATION AMOUNT

Precipitation composition in the UK is monitored using weekly bulk collectors at a network of 32 rural sites. Monitoring commenced in 1986 and data are reported annually (e.g. Vincent et al., 1995). The sites are generally remote with few local sources, although two sites are within 1 kilometre of a major road (>25,000 vehicles per day). Daily wet-only measurements of rainfall composition have also been made at five of the sites since 1987.

The validity of the weekly bulk collector measurements has been assessed by comparing the results from this collector with those from the daily wet-only collectors and generally good agreement has been found between the two types of collector (Stedman et al., 1990). Assessment of the larger dataset now available shows that measured concentrations of non-marine sulphate, nitrate and ammonium measured by the weekly bulk collector tend to be larger than those measured by the wet-only collector by up to 10% at the more polluted sites. The dry deposition of non-marine calcium is also significant at some sites. However, data from five wet-only collectors are insufficient to map precipitation composition over the UK and there are insufficient data to apply a correction to the maps derived from bulk collectors.

Precipitation weighted mean ionic concentrations have been calculated for each of the 32 sites in the network. Maps of these mean concentrations have been calculated by interpolation from the site means, either by the geostatistical method of kriging (hydrogen ion, non-marine sulphate, sulphate, nitrate and ammonium) or by bilinear interpolation (all other ions). The 32 monitoring stations for concentrations of major ions have proved adequate to obtain estimates of the broad spatial pattern of mean concentration throughout the UK. These patterns vary slowly across the country with differences in the annual volume weighted mean remaining quite stable between years.

It should be noted that there appears to be high concentrations of magnesium in the north and west of Scotland and in Northern Ireland. This is a reflection of the problems of adjusting for sea salt fractions with high sea salt deposition and low anthropogenic deposition. It does not indicate a real pollution effect in these areas.

Precipitation amount by contrast shows a very high spatial variability with in excess of 3000 mm in parts of the uplands of north west Britain and as little as 500 mm in the driest parts of East Anglia and the south east of England. As precipitation amounts for the UK are provided by an extensive network of rain gauges (in excess of 4500 collectors), the annual UK precipitation field is much better defined by the Meteorological Office data and interpolation than by the very limited number of collectors in the rainfall chemistry network.

MAPPING WET DEPOSITION TO THE UK TAKING ACCOUNT OF THE SEEDER FEEDER EFFECT

In the third report of the Review Group on Acid Rain (RGAR, 1990), the wet deposition maps for the UK were calculated as the product of Meteorological Office precipitation field and the volume weighted concentrations from the secondary network. The procedure has now been modified to take account of the enhanced concentrations of dissolved ions in the rainfall when low-level orographic enhancement by the seeder feeder process occurs (Carruthers & Choularton, 1984). This process operates over upland areas of the UK during periods of frontal rainfall with geostrophic windspeeds greater than 5 m s^{-1}. It is estimated that more than 80% of the annual precipitation occurs in these conditions in upland areas over the UK.

THE BASIS FOR THE MAPPING

Observations at Great Dun Fell (a remote rural site in Cumbria) covering 20 rainfall events, in a variety of weather conditions, over a period of two years, showed an increase in rainfall rate between the Eden Valley (200 m above sea level (asl)) and the summit of Great Dun Fell (850 m asl) of a factor of two. There was also an increase of a factor of between two and three in the concentrations of the sulphate, hydrogen and nitrate ions (Fowler et al., 1988). This was due to the seeder rain from aloft sweeping out cloud droplets from the capping (feeder) cloud formed as air was forced to rise over the hill. When this cloud was sampled at the surface it was always found to have a concentration of these ions substantially in excess of those in the rain. The increased concentrations of these ions in the rainfall at the summit of the hill, compared to the valley floor, imply that on average the concentrations in the additional rain (from the feeder cloud water) were a factor of three to four times higher than in the seeder rain.

There are two main reasons for the higher concentrations of ions in the cap cloud water compared to the seeder rain: firstly in the UK the concentrations of non-marine ions tend to be higher in the atmospheric boundary layer than in the free troposphere where the seeder rain forms. This is due to strong surface sources of a range of species associated with anthropogenic activity. When the boundary layer air is forced to rise over the hill the cap clouds form on the atmospheric aerosol containing the soluble particulate material. Soluble trace gases will also then dissolve in the cloud water contributing to the soluble mass to be scavenged and wet deposited; the second process is that when the seeder feeder mechanism is operating the seeder rain is usually produced by the vapour growth of snow flakes in the seeder cloud. This is very inefficient at removing the dissolved particulate in cloud droplets. These snowflakes melt to form rain as they descend to lower levels with temperatures above 0°C. These raindrops will then very efficiently scavenge the cloud droplets in the feeder cloud by collision coalescence.

Case studies performed over a larger region of complex topography (Dore et al., 1990) have shown, in agreement with model predictions, that the gain of these ions by scavenging generally produced a rather smaller enhancement in concentration than observed in the studies described above. Further, these results show that the enhancement of concentration of these ions in rain caused by scavenging of the feeder cloud is quite variable, typically between 1.5 and 3, depending on rainfall rate, wind directions, windspeed etc. Based on these results a typical global figure of a factor of 2 was taken for the preparation of the map. The paucity of data in elevated regions suggests that it is probably not appropriate to attempt to refine this to individual areas. It is, however, a somewhat conservative estimate and is likely to produce a significant under-estimate of wet deposition in some areas as discussed below.

MAPPING WET DEPOSITION

To generate the map of wet deposition, the first requirement is to establish the base rainfall, that is the rainfall which would have occurred at any location if the country had been flat and therefore no seeder-feeder effect had occurred. Taking the coastal rainfall at the west coast as the base rainfall near the coast and likewise at the east coast, a linear interpolation across a west east transect provides the first approximation to the base rainfall. If an area of the transect receives rainfall less than the first approximation to the base rainfall, a second approximation using piecewise linear interpolation is constructed. This second approximation is principally required when a substantial area receives rainfall lower than the east coast rainfall, for example in the western parts of Cambridgeshire.

Having established the base rainfall, it is assumed that the additional rainfall is feeder enhanced rainfall and has a higher concentration of the major ions than estimated from the interpolated rainfall ion concentration maps. The monitored data used for the interpolations are generally collected at relatively low-level locations where rainfall amounts are similar to the base rainfall. As discussed above, the concentration of ions in the feeder rain was assumed everywhere to be twice that in the interpolated rainfall. This procedure is a modification of that used for the original seeder-feeder enhanced UK wet deposition maps (Dore et al., 1992).

TESTING THE MAP

A series of field projects has been conducted in areas where high deposition by rainfall is predicted to occur. These include sites in the north-west Highlands of Scotland, the South Pennines (Inglis et al., 1995a) and North Wales. In addition continuous monitoring of cloud and rainfall composition has been available from Dunslair Heights, Halladale, Great Dun Fell and Holme Moss covering the last 3 years. The results from these field monitoring studies are briefly described in Fowler et al., (1995a) and Inglis et al., (1995b) and are discussed in detail in the fourth report of the Review Group on Acid Rain (RGAR, 1997). In summary, these studies give strong support for the choice of a factor of 2 for the concentration enhancement in the feeder rain for national mapping of the wet deposition of major ions (NH_4^+, SO_4^{2-}, NO_3 and Cl^-). Some variation from this factor is apparent with higher values for sea-salt ions over hills very close to the coast and for other ions downwind of nearby source regions e.g. ammonium downwind of agricultural areas, but the modification of the wet deposition map for these effects is not currently implemented.

The modelled deposition estimates obtained for short-term monitoring data have been confirmed by the study of inventories of an isotope of lead (^{210}Pb) in soil. The radionuclide ^{210}Pb derived from gaseous radon (^{222}Rn) is present in particle form in the atmosphere attached to the same aerosols which contain the bulk of the pollutant sulphur and nitrogen. When scavenged from the atmosphere by precipitation, the ^{210}Pb is readily attached to organic matter in the surface horizons of soil. The inventory of ^{210}Pb in soil can be used to measure the spatial variation in wet (or cloud) deposition within a region due to orography or land use, averaged over several decades (half life of ^{210}Pb is 22.3 years). This technique, developed by Mourne (1993), has been used to study the orographic enhancement at a range of UK sites. For example, at the hill summit of Great Dun Fell in Cumbria, (~850 m asl) precipitation of approximately 2000 mm yr^{-1} exceeds that on the low ground upwind by a factor of 2.0. The inventory of ^{210}Pb increases along the same transect by a factor of 3.3, due to seeder-feeder scavenging of orographic cloud. The measurements show that the average ratio of concentrations in scavenged orographic cloud to rain upwind of the hills is 2.2 (Fowler et al., 1995b). These data are entirely consistent with the studies of the variation in major ion concentration with altitude at Great Dun Fell and elsewhere.

Cloud deposition

INTRODUCTION

Many studies (Dollard et al., 1983; Fowler et al., 1995a) in the UK have shown that much larger concentrations of all major ions are found in hill cloud than in precipitation. The ratios of ion concentration in hill cloud to that in precipitation are variable but range from 2 to 20 with mean values of typically 5 for SO_4^{2-} and NO_3^- in the UK uplands. On occasions with polluted continental air advected over a cool North Sea, the concentrations of the major ions in hill cloud on the uplands of the east coast may reach 1 to 2 mM, concentrations which have been shown to cause damage to several conifer species (Sheppard, 1994; Cape, 1993). Furthermore, the aerodynamically rough nature of forests may considerably enhance the deposition of cloud droplets in the uplands of the UK, so that land use influences pollutant inputs to catchments through cloud droplet deposition. For these reasons it is important to quantify the contribution of cloud deposition to total inputs throughout the UK, and to identify the sites and catchments where the exposure to polluted hill cloud represents a threat to the vitality of the forest canopy or to the ground foliage.

OBJECTIVELY-ANALYSED CLOUD IMMERSION FREQUENCIES FOR THE UK

In the UK very few meteorological observation sites are at elevations above 300 m asl so that direct data on cloud immersion are scarce. Moreover, the pattern of cloud immersion frequency is likely to be of a scale equal to or smaller than that of the orography, so that a prohibitively large number of stations would be required to define the pattern explicitly.

It is clear from the foregoing discussion that direct observations of cloud immersion are grossly inadequate to define the pattern over a topographically-complex area such as the UK, so use must be made of proxy data.

APPROACH TO THE ANALYSIS

Under many meteorological conditions the air below cloud base is well-mixed (either because of convection or due to frictionally-generated turbulence) and the level of cloud base is almost uniform, even over hills where orographic lifting of low-level air takes place. However, when the lowlevel air is thermally stable, orographic lifting will normally lead to the level of cloud base being lower over the windward side of hills than the general level of cloud base. On occasions when precipitation occurs over the hill-tops, cloud base will normally be higher over leeward slopes than windward slopes. Nevertheless the assumption that average statistics on the level of cloud base have a relatively large spatial scale is reasonably valid, so that these statistics can be used to infer cloud immersion statistics by assuming that the underlying orography is immersed passively in the cloud, without either affecting the cloud base level or the cloud amount.

A standard statistic derived from cloud observations made at meteorological stations is the percentage of time that the sky has cloud cover of 5/8 or more at various specific heights. At Royal Air Force stations the statistics are for 3/8 or more cloud cover. These cloud base data for a 20-year period from a total of 100 stations in the UK were used to determine 3 dimensional frequency fields of cloud cover (Weston, 1992). The analysis used orthogonal polynomials as base functions (Dixon et al., 1972), but to increase the accuracy of the representation in the vertical, the data were split into three overlapping sets covering the height ranges 0-250 m, 150-600 m and 350-1500 m. Polynomials were evaluated to third order in all three dimensions, so that the analysed fields were represented by 20 coefficients.

RESULTS

The results of this analysis can be used to derive cloud immersion frequencies on any spatial scale for which land height data are available. For the UK, highest immersion frequencies occur over the Cairngorm Mountains, where there are several peaks of over 1200 m. The immersion frequency, given by the analysis, for the highest summit in the Cairngorms (Ben MacDhui, 1309 m) is 42%.

CLOUD COMPOSITION

There is no formal network of cloud water samplers in the UK (or any other country), but from the beginning of the mechanistic studies of orographic enhancement at Great Dun Fell (1984), campaign measurements of cloud water using passive collectors have been made. In addition, a range of measurements of cloud water using the lidded passive collectors at a range of UK sites have been made throughout the uplands of the west and north (RGAR, 1997). Since 1992, two sites have monitored cloud chemistry continuously as a part of the Department of Environment Air Quality Research programme. The two sites, Dunslair Heights at an elevation of 600 m asl in the Scottish Borders and Holme Moss (550 asl) in the Southern Pennines, provide cloud frequency, cloud chemistry and rain chemistry. These two sites are primarily used to provide long term data and validate the current models of cloud frequency and deposition.

There are therefore widely separated locations within the UK with cloud water chemistry measurements to demonstrate the geographical distribution in cloud composition and two sites with long term averages.

The measurements show average concentrations in the range 100 to 400 µM SO_4^{2-}, NO_3 and $NH_4^{+.}$ For some episodes 2-3 mM $SO_4{}^{2-}$, NO_3 and NH_4^+ concentrations are observed, with samples black with carbonaceous particles (Hadi et al., 1995). Such episodes occur when polluted continental air carrying large concentrations of the major ions in aerosol form is advected over the North Sea. The aerosols are readily activated into cloud droplets either in the stratiform cloud formed over the sea or in orographic cloud over the UK. These cloud droplets are then deposited to vegetation in the uplands and rates of deposition on forests are particularly large being limited only by rates of turbulent transfer (Gallagher et al., 1991).

CLOUD DEPOSITION

The field measurements of cloud droplet deposition onto moorland and forests showed the rates of deposition to be very similar to the rates of momentum transfer for the droplet size range 4µm to 20µm (radius) (Beswick et al., 1991). This size range contains the bulk of the cloud water and thus provides a very convenient surrogate to estimate rates of cloud water deposition to terrestrial surfaces (Fowler et al., 1991). The rates of momentum transfer and hence cloud droplet deposition may be estimated directly from a knowledge of the roughness length (z_0) and wind velocity over the vegetation. Corrections should be applied for the effects of vertical profiles of temperature but in practice the conditions associated with cloud deposition in the uplands of the UK are not those in which significant corrections for stability are necessary. Maps of land use and wind velocity can therefore be used to calculate the deposition rate for cloud water.

To calculate the cloud deposition inputs of the major ions it is necessary to know the ion concentration as well as the deposition rate. The orographic effects lead to marked vertical gradients in ion concentration with altitude. However, as the bulk of aerosol mass entering cloud base is effectively activated to cloud droplets at that level and as the vertical gradient in concentration arises purely as a consequence of the increase in cloud liquid water content with altitude, then the concentration of the major ions per unit volume of air remains almost constant with altitude within the cloud. Therefore cloud droplet deposition can effectively be calculated by using the ion concentration per unit volume of air and the deposition rate for momentum transfer for droplets in the appropriate size range. The concentration field is taken from the values interpolated from the secondary network measurements multiplied by the average measured ratio of ion concentration in orographic cloud to that in rain.

Dry deposition

SULPHUR DIOXIDE

Mapping concentration

As a large proportion of UK emissions of sulphur dioxide is emitted from tall stacks, the mean ground level concentration is a relatively smoothly varying function. The largest mean concentrations occur in Central England, in the area where there are several large power stations, and concentrations tend to decrease in all directions away from this region. There are also smaller maxima in the spatial distribution in Central Scotland, South Wales, the Thames Estuary and Northern Ireland.

Where there are low-level sources, around particular industrial sources, close to major roads or in areas where buildings are heated by burning sulphur-containing fuels, mean concentrations are locally elevated. For example, examination of data from urban monitoring networks clearly shows that urban areas in regions such as Northern Ireland and South Yorkshire have larger densities of local sources of sulphur dioxide than elsewhere.

In deriving maps of sulphur dioxide concentration, data have been used from the DoE Rural Sulphur Dioxide Network (Downing and Campbell, 1995), DoE Rural Automatic Networks (Bower et al., 1994) and from National Power and PowerGen (Webb and Jenkin, pers. comm.). Annual mean values at the sites were interpolated on to a 20 km grid using the geostatistical technique of kriging (Webster et al., 1991).

To map the concentration in and around urban areas the approach taken is to represent the concentration in urban areas as a sum of the contribution from remote (>10 km) sources, derived from the interpolated rural maps, and a local contribution derived from a simple "box" model using a gridded emissions inventory.

In a simple box model, the local contribution to the mean concentration, c, is given by:

$$c = q / dhu$$

where q is the emission rate from a grid square of length d, u the wind speed and h is a height scale factor to represent vertical dispersion. The height scale factor is dependent on wind speed, the size of the grid square and vertical diffusivity and is difficult to predict. We have therefore used an empirical approach in which the factor:

$$1/dhu$$

is derived empirically from measurements of concentration and emissions estimates.

For sulphur dioxide, emissions estimates are available at a 10 km x 10 km resolution from the National Atmospheric Emissions Inventory (Salway et al., 1996). Annual mean sulphur dioxide concentration data were available for at least one year between 1992 to 1995 for 136 sites in the Basic Urban Network (UK Smoke and Sulphur Dioxide Monitoring Networks, 1995). The difference between Basic Urban Network values and the interpolated rural value was calculated and this was assumed to be solely due to the impact of local low-level emissions. This difference was compared to low-level emissions from the 10 km x 10 km square containing the site.

There were many sites for which the measured concentrations were larger than would be expected from the emissions estimate, although there were also a few for which the measured concentration was smaller than expected. This is largely due to the nature of the Basic Urban Network which includes many sites in smaller urban areas where domestic coal emissions are still significant. Emissions densities around these sites will be larger than the average for the 10 km x 10 km grid square. A more robust relationship was obtained by taking a small subset of 9 sites in the most urban environments (>60% urban/suburban land cover in the 5 km x 5 km grid square containing the site) (Fuller et al., 1994).

Using linear regression, the following relationship was derived:

$SO_2 = SO_2\,(\text{rural}) + 0.001q_{10}$

ppb   ppb

where [SO_2 (rural)] is the interpolated rural concentration and q_{10} is the 1994 sulphur dioxide emissions in tonnes from 10 km x 10 km grid squares, excluding large point sources.

This relationship was then used to map SO_2 across the UK using the national emissions dataset and the interpolated rural. This "budget" map represents the grid square mean concentration, including the contribution from within-square low-level emissions.

Dry deposition

Dry deposition is mapped using a process-based model to simulate transport of the gas to a surface and then uptake of the gas by leaf surfaces, stomata, soil and water surfaces (Smith et al., 1995). In order to calculate SO_2 deposition velocities (Cape et al., 1991) a resistance analogy is used with three resistances in series: an aerodynamic resistance (R_a), a quasi-laminar boundary layer resistance (R_b) and a plant canopy resistance (R_e).

The first two resistances, R_a and R_b determine the transport of the gas from the boundary layer atmosphere to the surface and are dependent on wind speed, the height of the surface above the ground and the roughness length of the surface. All surfaces are treated as vegetation and the plant canopy concept is used throughout the model. To determine the height of the canopy and its roughness length, the whole UK land area is categorised into 5 land cover types (arable, forest, grassland, moorland and urban) using survey data, map data and satellite images (Howard & Bunce, 1995; Fuller et al., 1994). Typical monthly values of canopy height are used for each land cover type and the roughness length is determined from the canopy height.

The plant canopy resistance, R_c is a combination in parallel of a stomatal resistance (R_s) and the surface uptake resistance representing leaf surface, soil and water surface absorption. Incoming solar radiation, temperature and vegetation type all determine the value of R_s, which is modelled hourly for a typical day in each month under clear sky and overcast sky conditions. The combined surface uptake resistances are simplified to take only two values, one for dry surfaces and one for wet surfaces. Data on cloud cover and rainfall are used to combine these components in appropriate proportions to model R_c for each land cover type for each month of the year.

The deposition velocity is determined from R_a, R_b and R_c, for each land cover type and then values for the 20 km x 20 km squares are weighted averages depending on the proportions of land cover type in each square. The monthly, and hence annual, sulphur deposition is calculated by multiplying the deposition velocities and the interpolated SO_2 concentration field. All the meteorological data used in this model are 30-year climatological averages provided as 40 km x 40 km spatial averages (Thompson et al., 1982), as location data or as interpolated maps (Page and Lebens, 1986).

NITROGEN DIOXIDE

NO_2 Concentration map

The nitrogen dioxide maps were derived from measurements using diffusion tubes, a method for which there is some disagreement in the literature about accuracy and precision. However, while this method is less precise and accurate than instrumental monitoring methods, it is adequate for the estimation of annual mean concentrations at rural sites to within 1 ppb or 10-15%, especially where the laboratory concerned undertakes regular comparisons against active sampling methods.

Diffusion tubes are used to monitor nitrogen dioxide concentrations at the rural precipitation composition monitoring sites. In addition, automatic monitors using the chemiluminescence produced when nitrogen oxide reacts with ozone to detect NO_x are used at three sites (Lullington Heath, Ladybower and Strathvaich Dam).

For urban background NO_2 which, like urban SO_2, varies at much finer spatial scale than 10 km x 10 km, surrogate data rather than published emissions estimates were used in mapping. Emissions from major roads have been estimated on an individual road link basis using standard National Atmospheric Emissions Inventory methods and Department of Transport traffic flow data. Other urban emissions have been modelled using 1 km x 1 km land use data and have been assumed to be proportional to the percentage of urban and suburban land cover in each grid square (Fuller et al., 1994).

Using a regression analysis of the relationship between the local contribution to mean nitrogen dioxide concentration at Automatic Monitoring Network sites (derived as for SO_2, from the difference between the measurement and the interpolated rural value) and these surrogate statistics the following relationship was derived:

$$NO_2 \, / \, ppb = NO_2 \, (rural) / \, ppb + 0.2135 \, q_u + 0.0017 \, q_r$$

where q_u is the percentage urban and suburban land cover in the 5 km x 5 km grid square and q_r is the emission from major roadworks in the 5 km x 5 km grid square in tonnes as NO_2.

This relationship, together with national maps of q_u and q_r was used to produce a `budget' map to represent the grid square average concentrations, including the contribution of local low-level sources.

NO_2 Deposition

The dry deposition of NO_2 is calculated using a similar model to that used for SO_2. The major difference for NO_2 is that stomatal uptake is the major deposition pathway and the only one modelled. Internal (mesophyll) resistance is assumed to be negligible as has been demonstrated in detailed laboratory studies. The leaf surface (cuticular) deposition pathway is taken to be a very weak sink, since the literature on NO_2 deposition shows values for nonstomatal uptake equivalent to only 0.5 to 1.0 mm s^{-1}. In addition minor corrections to the atmospheric and quasi-laminar leaf boundary layer resistances and the stomatal resistance are introduced to correct for the different molecular absorption sites of SO_2 and NO_2.

AMMONIA

Mapping ammonia concentrations

Although emissions of ammonia are widely distributed in rural areas, because of the ground level nature of the emissions from agricultural sources, there is a high spatial variability in NH_3 concentrations, especially in source areas. This is important, since the sources are often located in close proximity to sensitive ecosystems acting as receptors for NH_3 deposition. Particularly at risk from locally elevated NH_3 concentrations are small woodland, grassland or moorland nature reserves located in intensive agricultural landscapes. In contrast, NH_3 concentrations are expected to decline rapidly in remote non-agricultural areas to rather uniform and small air concentrations. In these situations a much lower density of monitoring sites is required to identify representative air concentrations.

The NH3 concentration field at a 5 km x 5 km grid resolution of ground level NH3 concentrations is provided by the FRAME (Fine Resolution Ammonia Exchange) model of Singles et al., (1997). A key input to the model is the estimated distribution of NH_3 emissions of Dragosits et al., (1996). FRAME is a multi-layer coupled chemistry model based on developments from the TERN (Transport over Europe of Reduced Nitrogen) model (ApSimon et al., 1994), and is one of several models that were compared by RGAR (1997). The estimated air concentration field indicates a substantial variability in NH_3 concentrations, broadly supporting the patterns of the diffusion tube estimates, except that the model indicates much smaller concentrations in remote areas. The advantage of the model estimate is that it provides a much more detailed indication of expected spatial variability, than would ever be possible by measurements alone. On the other hand, it must be recognized that there are uncertainties in both the emissions data and the modelling.

Recently a new DOE ammonia monitoring network has been set up, which includes improved sampling techniques.

Mapping ammonia dry deposition

The dry deposition of NH_3 is calculated using a modification of the modelling developed for SO_2 and NO_2. In the case of NH_3 over many land surfaces, particularly agricultural ecosystems, fluxes are bi-directional with both emission and deposition occurring (Sutton et al., 1993, 1995). Although there is evidence that bi-directional fluxes may partly be due to adsorption/desorption effects (Sutton et al., 1997), a major underlying control is the existence of the NH_3 compensation point χ_s). This is the concentration of NH_3 occurring in equilibrium with plant tissues within plant stomata; when air concentrations are less than χ_s, emission is expected whereas deposition occurs when air concentrations are larger. The exchange process is however complicated since NH_3 is very soluble and often deposits rapidly to leaf cuticles. The consequence is a competition between cuticular and stomatal exchange processes.

Ammonia compensation points are related to the level of agricultural intensification of plant communities, such as fertilizer input, as well as temperature, plant phenology, and even, for semi-natural plants, total atmospheric nitrogen inputs (Sutton et al., 1995). The evidence suggests a broad distinction with larger values for agricultural croplands and grasslands. The smaller values for semi-natural land mean that, while emission can sometimes occur, the net flux is dominated by deposition.

At present, values of χ_s for semi-natural land are the subject of substantial uncertainty, and the present modelling approach for the UK applies the compensation point modelling approach only for croplands and grasslands. In this case diurnal patterns of NH_3 exchange are predicted which vary monthly and spatially in relation to climate over the UK. The model has been applied with the mapped NH_3 air concentration field together with spatially varying climate inputs. So far mapping has been limited to a 20 km x 20 km grid resolution, and an example map for arable land has been presented by RGAR (1990). For semi-natural moorlands and forests the more usual canopy resistance model is still applied. Available earlier measurements in the UK and Europe indicated rather rapid rates of NH_3 dry deposition to semi-natural ecosystems (Sutton et al., 1993, Duyzer et al., 1994), though more recent and extensive datasets indicate that substantial canopy resistances for NH_3 can often occur (e.g. Wyers & Erisman, 1997; Fowler et al., 1997). In the present modelling, these results are summarized using a canopy resistance of 20 s m^{-1} for moorlands and forests, which provides slightly smaller deposition velocities than estimated for INDITE (1994).

Since NH_3 deposition rates are so intimately connected to differences in ecosystem type and management, it is important to recognize that there is not a single simple map of NH_3 dry deposition for the country. Two classes of maps may be prepared: a) maps of NH_3 inputs received by particular ecosystem types (kg N ha $^{-1}$ yr^{-1}); b) budget maps of NH_3 deposition within particular grid squares. While the former indicates what would be received by an ecosystem if it occurred, the latter accounts for the area of the ecosystem for each square. The ecosystem receptor maps are most important for Critical Loads exceedances, since these provide the deposition estimates relevant for comparison with critical loads. Dry deposition of NH_3 received by moorlands and woodlands/forests can then be the estimated in Great Britain. The much larger estimated inputs to forests are a consequence of increased turbulence and hence larger deposition velocities compared with moorland vegetation, and this is obviously an important effect in defining critical load exceedances. There is only limited information on the rates of NH_3 deposition to other semi-natural low vegetation, such as unfertilized grasslands. The estimates for moorland have sometimes been applied as a best estimate for other low vegetation, but such estimates must be recognized as much more uncertain.

BASE CATION DEPOSITION

The dry deposition inputs of base cations are calculated as the product of air concentration of the aerosol base cations (Ca^{2+}, Mg^{2+}) and the dry deposition velocity appropriate for the mass mean diameter of these aerosols. While perfectly satisfactory as a procedure, there is a major problem with the input data as few direct measurements of base cation aerosol concentrations are made. Measurements of base cations in the UK are reported by Cawse et al., (1994) Lee et al., (1995) and Fowler et al., (1996). These data are not spatially representative of the UK as a whole and are not therefore appropriate for provision of a UK map of base cation dry deposition. To obtain the aerosol concentration field, concentrations of base cations in precipitation are used. The concentrations of base cations in precipitation are derived from the precipitation scavenging of aerosols, and therefore may be used to infer aerosol concentrations using the scavenging ratio (the ratio of the concentration per unit mass of rain to the concentration per unit mass of air at the surface) (Garland, 1978).

Assuming all the base cations in rain arise through wet scavenging and not by dry deposition on the rain collector, this procedure provides approximate annual aerosol air concentrations for the deposition modelling exercise. The deposition velocity is taken from the relationship between particle size and deposition velocity given by Slinn (1982) using a mass median aerosol diameter of 1.0 µm. The approach used here is indirect and requires direct measurements for confirmation, and more information on the size distribution of base cations in the UK. In the work described by Erisman & Draaijers (1996) the same procedure is adopted for the whole of Europe, and is well supported by a more extensive programme of aerosol measurements than exists in the UK.

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UNCERTAINTY ESTIMATES

Possible uncertainty in the estimates of total deposition of sulphur have been studied. The uncertainty in estimates of total deposition of nitrogen are likely to be much larger and have not been explored so far.

The deposition models are linear with respect to the input concentrations of SO_4^{2-} or SO_2 and errors in these interpolated concentration fields are transmitted directly into the predicted deposition fields.

The use of geostatistics in the interpolation and mapping of United Kingdom precipitation composition was described by Webster et al. (1991). The kriging method, being statistical in nature, provides an estimate of the precision of the interpolated estimates. The precision, expressed as twice the standard error in the interpolated kriging estimates can be mapped in the same way as concentration.

However, the error estimates have to be interpreted with some caution. `Simple' kriging has been used even though the marked trends in concentration in both sulphur dioxide and non-marine sulphate across the UK violates the assumption of constant expected value across the mapping domain. Tests of various methods for removing the trend showed that the concentrations maps were not greatly affected by subtraction of the trend before kriging but that error maps were affected.

Using data from 1986 to 1988, Smith et al. (1995) performed a crude analysis of the likely levels of uncertainty in the predicted deposition of sulphur given the estimated uncertainty in the inputs. Following a similar analysis and assuming an error in the rainfall estimate to a 20 km square of ±10% with the kriging errors taken from the more recent maps, the uncertainty (i.e. an approximate 95% confidence interval assuming a Normal distribution of residuals) in estimates of wet deposition is about ±20% rising to ±60% in high altitude, high rainfall areas. Using the kriging errors from the interpolated concentration maps of sulphur dioxide results in an uncertainty of ±30% of the annual mean concentration in central and eastern England rising to over 100% in the north-west of Scotland. Assuming an uncertainty in deposition velocity of ±20%, the overall uncertainty in dry deposition estimates would range from ±50% in central England to well over ±100% in many areas of Scotland. The major pathway for deposition varies in different areas of the UK with 70% as dry deposition in central England to 80% as wet deposition in north-west Scotland. Combining only the above two calculations to get an estimate of the uncertainty in total sulphur input to a 20 km square suggests a value of ±40% in central England increasing to ±70% on the west of Scotland and Wales.

The above estimates rely on an analysis of the likely causes of variation in the models combined with the error map from the kriging interpolation of the concentration field. For both wet and dry deposition, the kriging error is the dominant component of uncertainty and it increases substantially as the available information from the monitoring network reduces, as happens particularly in the north and west of Scotland. It should also be noted that the absolute values of deposition are smaller in remote areas and that large relative errors may still indicate quite small absolute errors. Until there is much more detailed monitoring of local variability, these estimates are indicative rather than accurate.

As discussed by Smith et al. (1995), the few catchment studies that are currently available suggest an uncertainty level of about ±30% in total sulphur input to areas of approximately the same size as a 20 km square. This value is rather less than the uncertainty level predicted above but indicates that uncertainties of about ±40% for most of the country rising to about ±60% towards the north and west are not unreasonable given current understanding of the processes. The error analysis which has been used here assumes symmetry.

BASE CATIONS

The main purpose of estimating total base cation deposition is to enable the net acidifying input to be calculated. The total base cation deposition is a sum of the deposition components of both non-marine calcium and non-marine magnesium. These components are summed using their concentrations in ion equivalents (moles of ionic charge), rather than their masses as the effect of calcium and magnesium in balancing acidifying deposition depends upon the ionic charge carried by these ions rather than their total mass.

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