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Spatial and temporal variability in the deposition of acidifying species in the UK between 1986 and 1997

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2.1 Introduction

Prior to 1985 monitoring of precipitation chemistry in the UK was limited to a small number of locations, and a range of different protocols were used. These scattered data showed that rainfall acidity was similar in the UK to that in Scandinavia (Fowler *et al.*, 1982; RGAR, 1983). However, it was not possible with the limited data and the range of protocols for collection and analysis to map rain chemistry over the UK, and deposition budgets for the major pollutants were highly speculative.

The UK monitoring network for precipitation chemistry was set up during the mid-1980s, following a recommendation of the Acid Deposition Review Group (1985), and provided the first complete map of wet deposition of pollution for the UK in 1986 (RGAR, 1990). The monitoring from 1986 to 1997 covers a period of marked changes in emission of the primary pollutant SO_2 in the UK, which declined from 1966 kT S in 1986 to 830 kT S in 1997 (Figure 2.1). Other pollutants which contribute to soil and catchment acidification include the oxides of nitrogen NO, and NO_2, which are oxidized to NO_3^- in the atmosphere and NH_3 which when deposited may acidify soils following uptake by, and incorporation into, vegetation. During the 11 years of the deposition monitoring networks, emissions of these pollutants in the UK have also changed but by a much smaller extent than SO_2 (Figure 2.2). Pollutant emissions from other countries of Europe also influence concentrations and deposition in the UK, and in these countries sulphur (and to a lesser extent NO_x) emissions have also declined (Figure 2.1).

The period of intensive measurements of deposition of acidity in the UK is short relative to the natural variability of the weather. The observed changes in atmospheric concentrations and deposition of the pollutant gases, SO_2 and NO_x, and their oxidation products in the atmosphere, SO_4^{2-} and NO_3^-, must therefore be considered in parallel with seasonal and annual variability in the weather during the same period. However, the changes in sulphur emissions are large in both absolute and relative terms, and follow important policy decisions within the UK and elsewhere in Europe.

This short chapter is therefore centred on an analysis of the available measurements to show the degree to which the emission reductions have modified the concentrations and deposition of acidifying pollutants in the UK. The context within this report is on freshwater composition and ultimately the biological and ecological health of the freshwaters within the UK. Wet deposition of acidic pollutants in the acid sensitive uplands of western and northern Britain is therefore the central aspect of the analysis.

The UKAWMN, established in 1988, provides a slightly shorter period of measurements with which to compare deposition and surface water chemistry patterns. This chapter briefly describes the available deposition measurements, the temporal and spatial patterns in annual deposition for the UK as a whole.

The deposition data show considerable inter-site variability in both concentration and deposition as a consequence of local orographic effects and interactions with local variability in weather. As the precipitation chemistry collectors are not, in general, located close to UKAWMN sites, comparisons of temporal patterns in deposition and concentration are best between UKAWMN regional trends and wet deposition trends at the same scale. Within the last year, four new deposition stations have been sited within or nearby the catchments of UKAWMN sites, and these should facilitate more detailed catchment specific comparisons in the future.

To provide the necessary perspective in the analysis, the temporal trends in the UK patterns of wet and dry deposition are compared with trends in emissions of the major pollutants. The focus of the

Table 2.1

Monitoring sites illustrated in Figure 2.3 for the DETR wet deposition network and the UKAWMN.

Wet deposition monitoring network sites

Map Legend	Site No	Name	East	North	SO_4^{2-} Group
WD3	5004	Stoke Ferry	5700	2988	1
WD7	5009	High Muffles	4776	4939	1
WD10	5023	Preston Montford	3432	3143	1
WD11	5024	Flatford Mill	6077	2333	1
WD18	5117	Thorganby	4676	4428	1
WD19	5118	Jenny Hurn	4816	3986	1
WD21	5120	Wardlow Hay Cop	4177	3739	1
WD22	5121	Bottesford	4797	3376	1
WD25	5127	Woburn	4964	2361	1
WD26	5129	Compton	4512	1804	1
WD27	5136	Driby	5386	3744	1
WD5	5007	Barcombe Mills	5437	1149	2
WD9	5011	Glen Dye	3642	7864	2
WD13	5106	Whiteadder	3644	6633	2
WD15	5109	Redesdale	3833	5954	2
WD16	5111	Bannisdale	3515	5043	2
WD17	5113	Cow Green Res.	3817	5298	2
WD29	5149	Hillsborough Forest	1369	5156	2
WD1	5002	Eskdalemuir	3235	6030	3
WD2	5003	Goonhilly	1723	214	3
WD6	5008	Yarner Wood	2786	789	3
WD14	5107	Loch Dee	2468	5779	3
WD20	5119	Beddgelert	2556	3518	3
WD23	5123	Tycanol Wood	2093	2364	3
WD24	5124	Llyn Brianne	2807	2492	3
WD28	5140	Achanarras	3151	9550	3
WD30	5150	Pumlumon	2823	2854	3
WD32	5152	Balquhidder	2545	7207	3
WD4	5006	Lough Navar	192	5212	4
WD8	5010	Strathvaich Dam	2347	8750	4
WD12	5103	River Mharcaidh	2876	8052	4
WD31	5151	Polloch	1792	7689	4

UKAWMN sites

Map Legend	Site No	Name	East	North
AW1	1	Loch Coire nan Arr	1808	8422
AW2	2	Allt a'Mharcaidh	2881	8045
AW3	3	Allt na Coire nan Con	1793	7688
AW4	4	Lochnagar	3253	7859
AW5	5	Loch Chon	2421	7068
AW6	6	Loch Tinker	2445	7068
AW7	7	Loch of Glenhead	245	5804
AW8	8	Loch Grannoch	2542	570
AW9	9	Dargall Lane	2449	5786
AW10	10	Scoat Tarn	3159	5104
AW11	11	Burnmoor Tarn	3184	5043
AW12	12	River Etherow	4116	3996
AW13	13	Old Lodge	5456	1294
AW14	14	Narrator Brook	2568	692
AW15	15	Llyn Llagi	2649	3493
AW16	16	Llyn Cwm Mynach	2678	3238
AW17	17	Afon Hafren	2844	2876
AW18	18	Afon Gwy	2824	2854
AW19	19	Beagh's Burn	1353	5879
AW20	20	Bencrom River	1405	4820
AW21	21	Blue Lough	1428	4825
AW22	22	Coneyglen Burn	791	5508

Table 2.2

UK sulphur emission and deposition 1986 to 1997 and the atmospheric budget over the country (all values ktonnes)

Year	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997
UK emissions	1966	1961	1923	1860	1882	1790	1753	1584	1354	1176	1014	830
I/Ps non-UK European	120	102	75	94	80	100	86	92	78	73	90	75
Dry deposition	262	246	234	227	201	231	185	187	159	123	125	102
Wet+cloud deposition	230	226	251	229	226	223	215	186	198	155	171	132
Total deposition	492	472	485	456	427	454	400	373	357	278	296	234
Exported emissions	1594	1591	1513	1498	1535	1436	1439	1303	1075	971	808	671

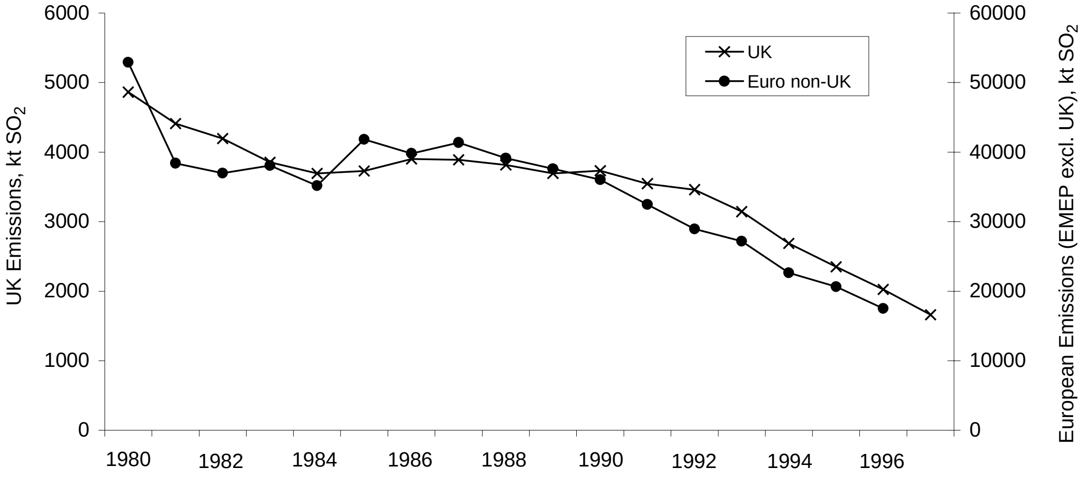


Figure 2.1

Trends in UK and non-UK European emissions of sulphur dioxide (1980-1997)

analysis presented in this chapter is an examination of all available evidence of deposition data and surface water chemistry data to show whether there is evidence of recovery. In short, have we detected a signal of reduced sulphur concentration or deposition in acid sensitive surface waters?

The Acid Deposition monitoring network is operated by NETCEN, while the wet and dry deposition maps for the UK are provided by ITE Edinburgh. This chapter has been prepared from the UK acid deposition monitoring data provided by NETCEN and the maps and process studies of ITE.

2.2 Wet and Dry Deposition

2.2.1 The wet deposition network

The composition of rain and snow is monitored at a rural network of 32 secondary sites using bulk collectors mounted 1.5 to 2.0 m above-ground sampled weekly and 5 primary sites using wet-only collectors sampled daily (RGAR, 1998). (Figure 2.3, Table 2.1).

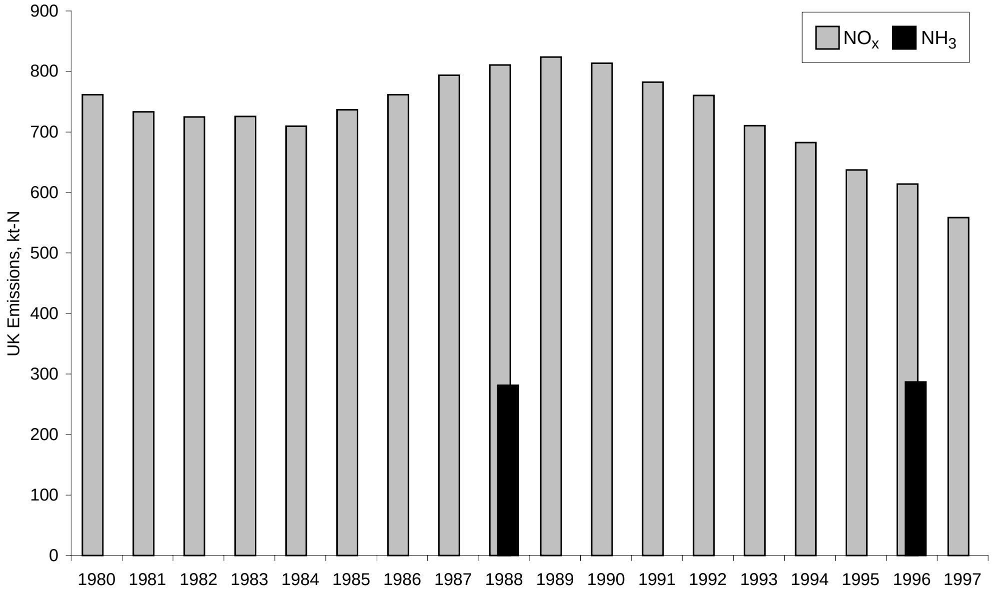
In general the monitoring sites are used to define the broad spatial patterns in rainfall composition. They do not sample the full range of the distribution of precipitation amount or composition. This is largely a practical constraint because the hill tops, where precipitation values are largest, are generally avoided as such sites are difficult to access in winter conditions, are very windy and a significant fraction of the annual deposition may occur as snow and is not collected efficiently. However, as Figure 2.3 shows, the monitoring sites cover the majority of the country and have proved suitable to define the regional distribution of precipitation chemistry (RGAR, 1998).

The weekly and daily samples are used to define the precipitation weighted annual mean concentrations of the major ions present in precipitation, SO_4^{2-}, NO_3^-, Cl^-, H^+, Na^+, NH_4^+, K^+, Ca_2^+ and Mg_2^+. These are then used to map the patterns of concentration. The mapping of precipitation weighted mean concentrations relies on Kriging methods (Webster *et al.*, 1991), assuming that the variation in space is locally random even though there is a spatial correlation.

Having mapped the precipitation weighted concentrations of each of the ions, the wet deposition is calculated as the product of the annual precipitation amount obtained from the UK Meteorological Office and provided at a scale of 5 km x 5 km. Met. Office data are used because the precipitation maps are constructed using a much larger network of gauges (in excess of 2000), which sample at ground level. The precipitation chemistry network relies on just 32 secondary sites and 5 primary sites and uses collectors mounted nearly 2 m above ground. The precipitation chemistry collectors have the advantage that they avoid some of the locally re-

Figure 2.2

Trends in UK emissions of NO_x between 1980 and 1997 and UK NH_3 emissions in 1988 and 1996



suspended contamination from soils but they under-catch precipitation amount because of the exposure of the collector to wind.

A further correction to the estimates of wet deposition is required because the Network does not adequately sample the high precipitation regions of the uplands where the wash-out of hill cloud by falling rain considerably increases wet deposition (Fowler *et al.*, 1988, 1995). The procedure used to modify the maps relies on empirical observations of the relationship between concentrations of major ions in orographic cloud and that of the upwind seeder rain (Dore *et al.*, 1992). The orographic enhancement of precipitation amount is assumed to occur entirely through seeder-feeder scavenging of orographic cloud.

The resulting maps of wet deposition were produced at a grid resolution of 20 km x 20 km from 1986 to 1994 and have recently been improved to 5 km x 5 km using a revised methodology which allows for the effects of wind-drift of falling raindrops.

2.2.1 Estimating dry deposition

The removal of the reactive pollutant gases at terrestrial surfaces by dry deposition represents the remaining major contributor to deposited acidity. Rates of dry deposition dominate the sulphur deposition inputs in regions with large ambient SO_2 concentrations (> 5 ppb) and modest rainfall (< 1000 mm). The rates of deposition are quantified using a deposition velocity ($V_{g(z)}$) at height (z):

$$V_{g(z)} = \text{flux/concentration}_{(z)}$$

and since concentration varies with height above ground as a consequence of deposition, the deposition velocity is also height dependent. The rate of dry deposition of SO_2 is regulated by stomatal uptake and leaf surface reaction of SO_2, especially in the presence of surface water on the vegetation, and is sensitive to the presence of other atmospheric pollutants notably NH_3 (Flechard *et al.*, 1999).

For the other acidifying pollutants, NO_2 and NH_3, rates of dry deposition are also regulated by surface processes. For NO_2 the deposition rate is primarily determined by stomatal absorption and overall rates of dry deposition are substantially smaller than those of SO_2 (Duyzer & Fowler, 1994). NH_3 by contrast is deposited rapidly on to most semi-natural vegetation (e.g. forest and moorland).

For NH_3, the surface-atmosphere exchange is

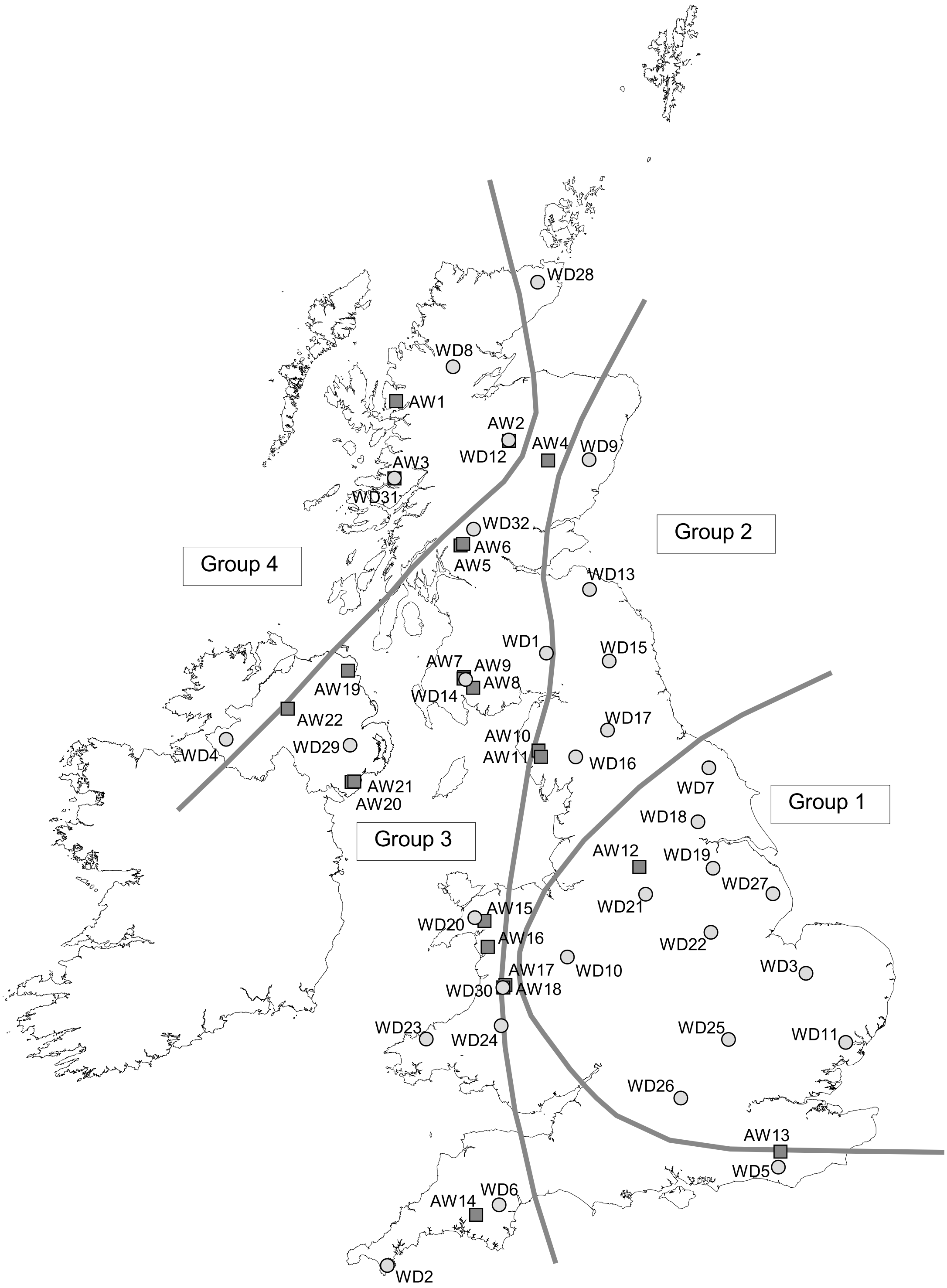


Figure 2.3

Locations of UK wet deposition monitoring stations (WD) and UKAWMN stations (AW)

The grouping of sites (1 to 4) is based on an objective hierarchical clustering method to distinguish the broad categories from the ionic composition alone (see Section 2.6)

Figure 2.4

Dry deposition of sulphur 1986 (a) and 1997 (b) from measured SO_2 concentration field and the ITE dry deposition model (Smith *et al*. 1999)

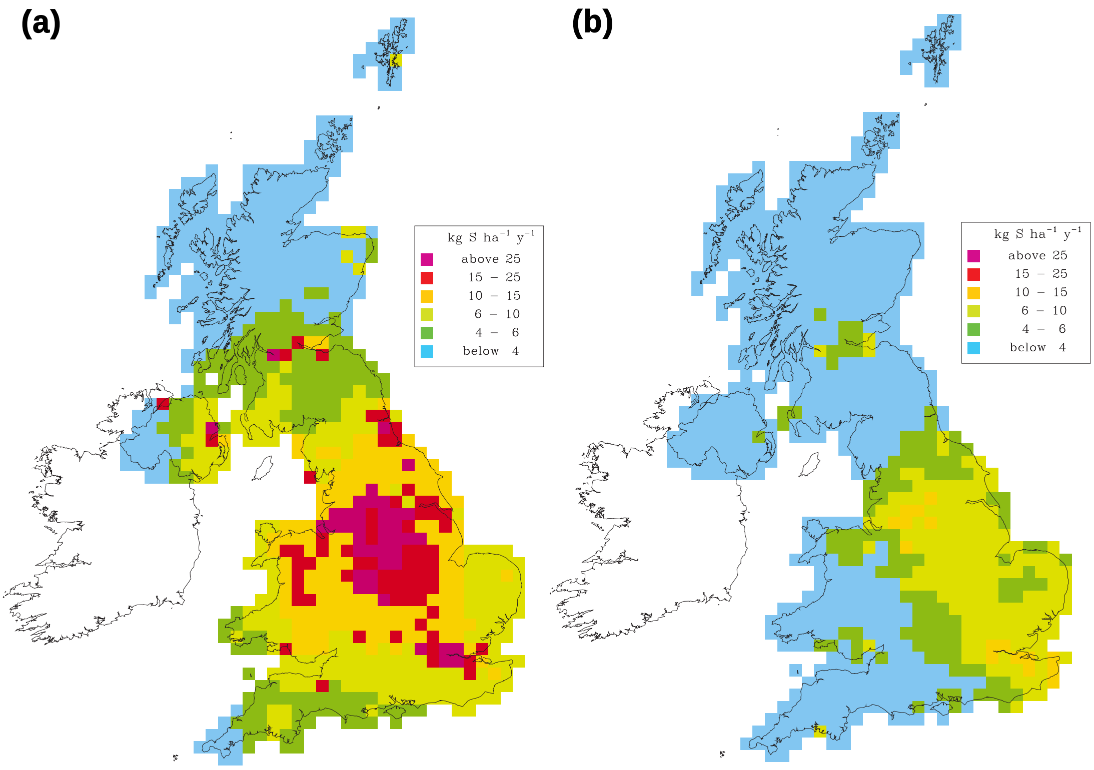
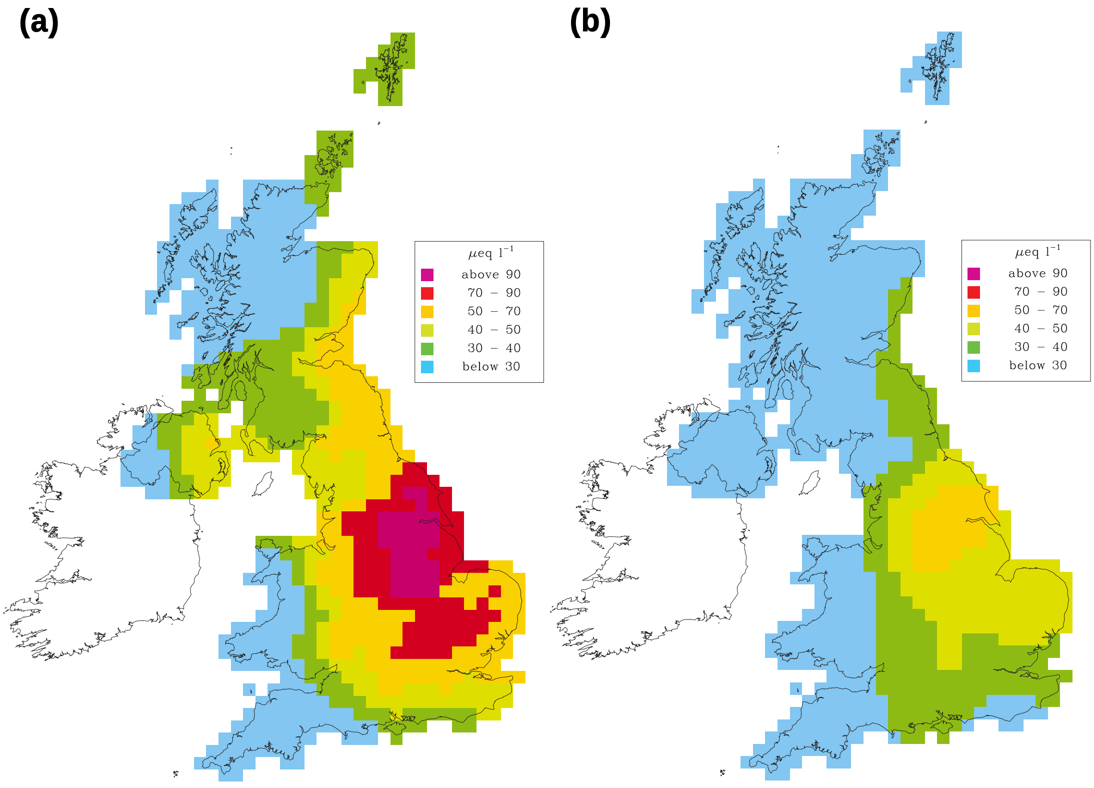


Figure 2.5

UK annual precipitation weighted mean concentrations of non-marine SO_4^{2-} in 1986 (a) and 1997 (b)



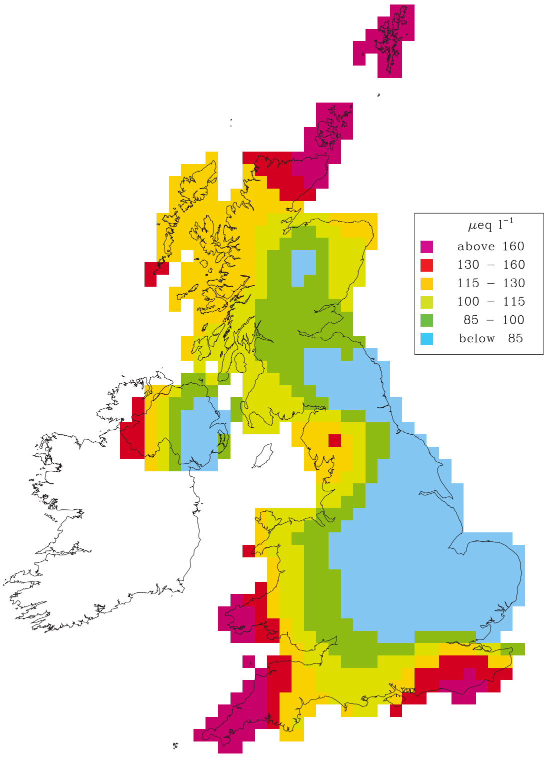


Figure 2.6

UK annual precipitation weighted mean concentration of Na^+ in 1997

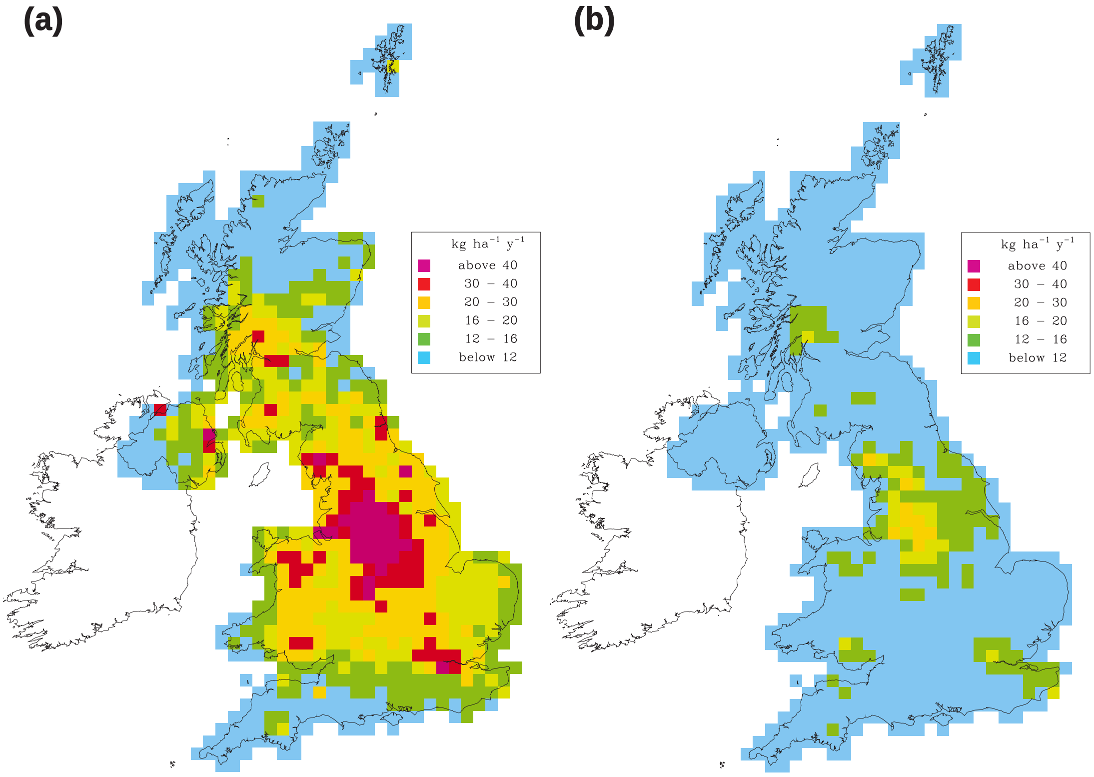
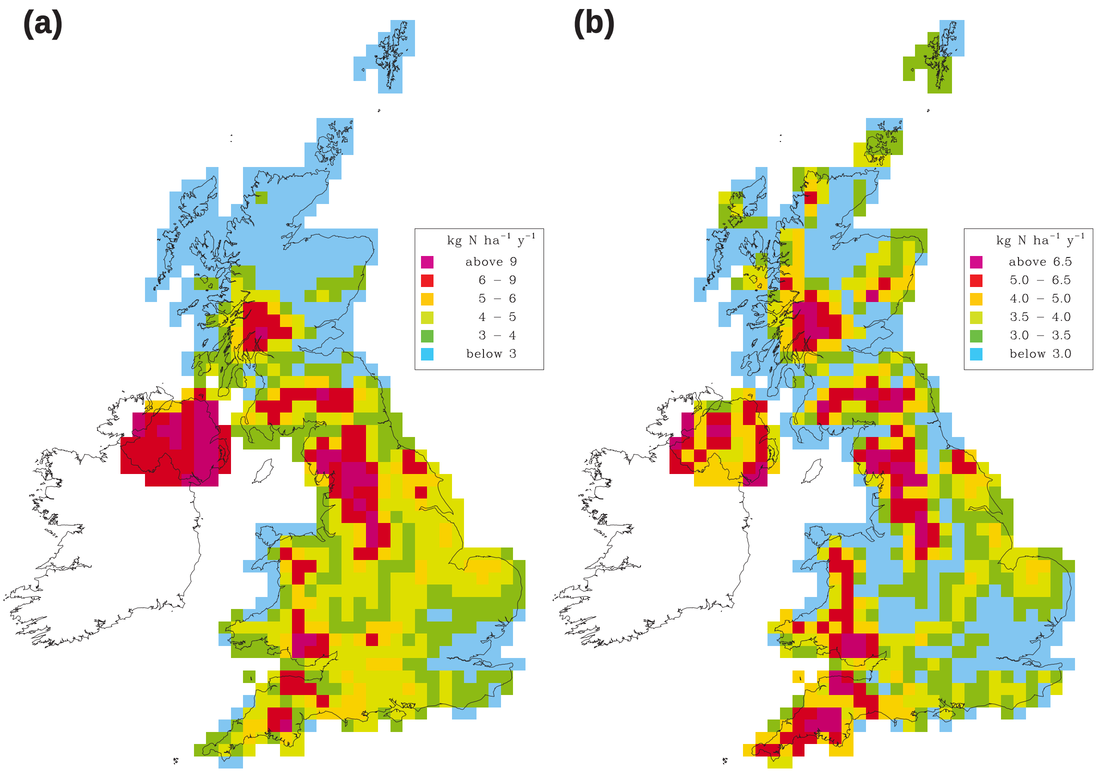


Figure 2.7

UK annual wet deposition of non-marine sulphur for 1986 (a) and 1997 (b)

Figure 2.8

UK annual wet deposition of NH_4^+ - N (a) and NO_3^- - N (b) for 1997



complicated by the bi-directional nature of the fluxes as a consequence of NH_4^+ within the apoplast of vegetation. For heavily fertilized crops the NH_3 fluxes may represent net emission over significant periods of the growing season, whereas semi-natural vegetation and forests represent an efficient sink for NH_3, with large deposition rates (Sutton *et al.*, 1993). A detailed treatment of the processes of dry deposition is outside the remit of this chapter and descriptions of the processes may be found in RGAR (1997) and in review papers e.g. Sutton *et al.* (1993) and Fowler *et al.* (1995).

The maps of dry deposition are provided by measured concentration fields of the pollutant gases and application of a process-based model of the deposition process (Smith *et al.*, 1999). The deposition is of course land-use specific, and land-use and land-cover maps are used to identify the major land-uses within the deposition grid (forest, moorland, unfertilized grassland, fertilized grassland, arable crops and urban areas). A more detailed description of the dry deposition measurement and modelling procedure is provided within the CLAG (fluxes) report (1997). Individual parameters within the deposition model and their response to changes in environmental conditions are provided by direct field measurements. There are two continuous SO_2 dry deposition sites within the UK and approximately 40 SO_2 concentration monitoring sites to provide the interpolated concentration fields for the UK.

The dry deposition of SO_2 to the UK is illustrated in Figure 2.4a for 1986 and 2.4b for 1997. The maps show a large change in the absolute values of dry deposition especially in the source areas of the east Midlands and Yorkshire. They also reveal the relatively small contribution of dry deposition in the areas of the west and north of the UK, which are the primary focus of the UKAWMN.

2.2.3 Cloud droplet deposition

Wet and dry deposition represent the dominant pathways for pollutant deposition, but for those areas of the landscape which are in cloud for a significant part of the time, the direct deposition of cloud droplets to vegetation represents an important contribution to the deposition total (Crossley *et al.*, 1992). For sites at altitudes above 600 m in western Britain the cloud frequency lies between 3 and 10%, and at forest sites above 500 m asl in the Scottish borders, 50% of the sulphur and nitrogen input may be deposited as cloud (or occult) deposition. The total deposition maps for acidity S and N for the UK include cloud deposition, although for the country as a whole cloud deposition is not a large component.

2.3 Measured wet and dry deposition, 1986 - 1997

2.3.1 Trends in concentrations

The concentrations of all major ions show large regional variation over the UK. For the pollutant derived SO_4^{2-} in the mid-1980s the largest concentrations were in the east and south of England with mean concentrations of 80-100 µeq l^{-1} and the smallest concentrations in northwest Scotland (15-20 µeq l^{-1}) (Figure 2.5a). The value of background SO_4^{2-} is of course important and is not known precisely. However, measurements at remote sites in northwest Europe from the EMEP network indicate values of the order of 10 ueq l^{-1}, so even the remote sites in the UK receive at least half of their non sea-salt SO_4^{2-} from pollutant sources. The current (1997) concentrations of non-marine SO_4^{2-} are shown in Figure 2.5b and these also show a large northwest to southeast gradient in the UK with values in northwest Scotland remaining close to 20 µeq l^{-1}, while the peak concentrations in the east Midlands of England have declined to about 60 µeq l^{-1} SO_4^{2-}. There is also a clear west to east gradient with larger concentrations along the east coast of the UK. The change in SO_4^{2-} concentration is dramatic and represents a reduction by almost 50% and is accompanied by a reduction in acidity of the same magnitude in the source regions.

The changes in SO_4^{2-} (and acidity) with time at sites on the west coast of the UK are small and largely non-significant.

The NH_4^+, NO_3^- and H^+ concentrations show similar spatial patterns with a marked east-west gradient and peak values in East Anglia. The absolute magnitude of the east-west gradient in NO_3^- concentration is similar to that in SO_4^{2-} i.e. 40-50 µeq NO_3^- l^{-1} across the country in the most polluted areas. However, the relative gradient is larger for NO_3^- because in the remote regions of northwest Scotland concentrations of NO_3^- were very small, typically 2-5 µeq NO_3^- l^{-1} in the mid 1980s. The values in the polluted areas of 40-50 µeq l^{-1} are therefore an order of magnitude larger than those at the remote sites. Differences between SO_4^{2-} and NO_3^- concentration gradients also arise because of the presence of a background in the SO_4^{2-} concentration. Sea-salt contains appreciable quantities of SO_4^{2-}, and in calculating non-marine SO_4^{2-} a correction is made for marine SO_4 by assuming the Cl^-:SO_4^{2-} and Na^+:SO_4^{2-} ratios in bulk sea water apply in the case of precipitation. At remote locations in the west and north of Britain this is a reasonable assumption, but in the east Midlands of England Cl is present as HCl and non-marine Cl^- in aerosols from the high Cl coals produced from some east Midlands coalfields. The marine correction for these areas relies on the Na^+:SO_4^{2-} ratio to quantify the non-marine Cl deposition.

There is also SO_4^{2-} in the atmosphere from marine emissions of dimethyl sulphide (DMS) which is oxidized in the atmosphere, ultimately to SO_4^{2-}, and contributes to non-anthropogenic background SO_4^{2-} deposition. The marked east-west gradients in concentrations of the major pollutant derived ions contrast strongly with the marine derived ions especially Na^+ and Cl^-. For these ions concentrations in the west coast sites are in the range 200 - 400 µeq l^{-1}, and sea salts dominate the ionic composition of precipitation and provide the majority of the total SO_4^{2-} deposition (Figure 2.6). The inland and east coast sites, in contrast, show marine Na^+ and Cl^- concentrations in the range 50-70 µeq l^{-1} and at these sites marine SO_4^{2-} contributes only 10% -

20% of total SO_4^{2-} in precipitation. The marine and pollutant derived ions therefore change in their relative contributions to the total ionic strength of the precipitation across the UK.

2.3.2 Trends in wet deposition

Combining the concentration fields with precipitation amount and correcting for the orographic effects in the UK uplands provides the wet deposition maps. As the precipitation amounts are very large in the uplands of western and northern Britain, the wet deposition maps show a stronger influence of precipitation amount than the concentration field.

The main features of the wet deposition maps are illustrated by maps for 1986 and 1997 for non-marine SO_4^{2-} (Figures 2.7a and 2.7b). The peak in wet deposition in 1997 of 25 kg non-marine S ha^{-1} in the Pennine hills of northern England and in Cumbria is appreciably smaller than non-marine SO_4^{2-} wet deposition in 1986 (50 kg SO_4^{2-}). The rainfall amounts do vary between years but are very similar for these years, and there are no monotonic regional trends in precipitation amount over the 12 year period. There are therefore areas of the country in which substantial reductions in deposition have occurred since the mid-1980s.

Wet deposition of non-marine S at west coast sites and in the north and west of Scotland shows no clear differences between the two years. Wet deposition of NO_3^- and NH_4^+ have also remained broadly similar although small changes are evident at individual sites. The spatial distributions in wet deposition of NH_4^+ and NO_3^- are shown in Figures 2.8a and 2.8b for 1997, again illustrating the dominance of the annual maps of precipitation in controlling the pattern of wet deposition.

■ 2.4 Trends in concentration and deposition: discussion

The main features of the regional patterns in wet deposition and the concentrations of major ions in precipitation have remained consistent throughout the monitoring period reported here, 1986-1987. However, the concentrations and deposition of sulphur have declined, with larger temporal gradients in the source regions than elsewhere. The trends in concentrations and deposition are much more important for interpretation of the UKAWMN data. For the trend analysis there are three key questions:

1. Have the reductions in UK (and other European) emissions of sulphur led to reduced S deposition in the UK and in particular in the source regions?
2. Are observed changes in concentration and deposition consistent with current understanding of the processes?
3. Is there evidence of changes other than in sulphur deposition in the UK precipitation chemistry and deposition?

The introductory section of this chapter and Figure 2.1, reveal a 57% decline in UK sulphur emissions between 1986 and 1997. Similarly, non-UK European S emissions declined by 45% between 1986 and 1997. These large changes provide an ideal signal to examine the measurement data.

Using a consistent methodology for the 12 year period, the mapped wet and dry deposition allow the mass balance of the atmosphere over the UK to be quantified. This is shown in Table 2.2. The total deposition of non-marine sulphur declines from 492 kT S in 1986 to 234 kT S in 1997, a reduction of 52%. The wet deposition declines by 42% while dry deposition declines by 61% over the 12 years, so there is a large change in the wet:dry deposition partitioning of the deposited sulphur in the UK. Clearly therefore, the answer to the first question is "yes", there has been a marked reduction in S deposition in response to emission reductions but the area in which deposition has declined is largely restricted to the source regions. Thus the answer to question 2 is "no", the observed change in deposition is unexpected. In particular the very large reduction in dry deposition, primarily as a consequence of a reduction in ambient SO_2 concentrations in the source region (within 100 km of the major sources), is the main cause of the much greater reduction in dry deposition. The concentrations of SO_2 declined by almost an order of magnitude at rural sites in the east Midlands.

The changes in the pattern of deposition and the partitioning into wet and dry deposition is therefore introducing non-linearity into the spatial relationship between emission and deposition of S in the UK. There are (at least) three contributions to the changes in wet-dry deposition partitioning. First, a much larger reduction in low level than high level sources of SO_2; second an observed change in the rate of SO_2 dry deposition which has gradually increased dry deposition rates in the source regions as SO_2 concentrations have fallen, and last; an oxidant limited SO_2 to SO_4^{2-} oxidation in stratiform cloud. All three processes have combined to cause the observed non-linearity in sulphur deposition but the relative contribution of each of these processes to the observed trend has yet to be quantified.

We now examine the trends in the different regions of the UK.

2.5 Regional trends in precipitation chemistry

A consequence of the smaller change in wet deposition is that the signal in declining SO_4^{2-} concentrations is smaller than it would have been given a strictly linear relationship between emissions and wet deposition, by 50%.

The observed decline in SO_4^{2-} concentration in precipitation (Appendix 1, Table 1) is clear at the sites in the east Midlands and Yorkshire - the source areas. In these areas (within 100 km of the major power stations) the non sea-salt SO_4^{2-} concentration declines at approximately 3 μeq SO_4^{2-} yr^{-1} throughout the 12 years and the (linear) trends are highly significant. At the sites close to the west coast of England, Wales and Scotland and in the west of Northern Ireland there is also a decline in non sea-salt SO_4^{2-}, but for each of these sites considered individually the decline is small and is not statistically significant. When all west coast sites are considered together, a small statistically significant linear trend of decreasing SO_4^{2-} is established.

The intermediate sites, including Eskdalemuir, Redesdale, Mharcaidh, Achanarras, Barcombe Mills and Compton show significant decreases in SO_4^{2-} averaging between 1 and 2 μeq SO_4^{2-} l^{-1} yr^{-1}. Thus the reduction in wet deposition is clearest in the same areas as the dry deposition reduction, and in fact the dry deposition on precipitation collectors contributes about 25% of the observed decline in wet SO_4^{2-} deposition in the source regions.

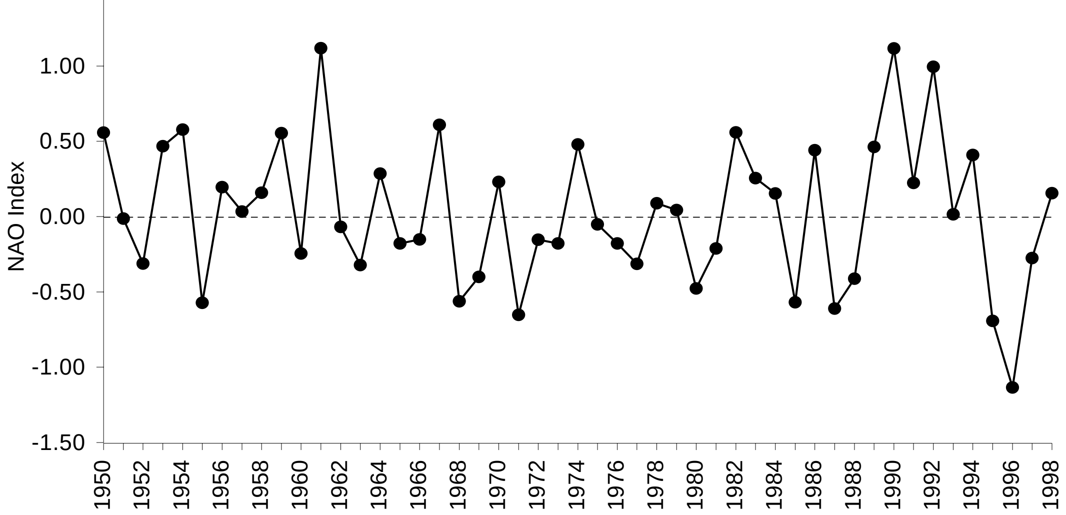
The trends are therefore weakest at the remote high rainfall sites and, in a strict sense, the observed decline in non sea-salt SO_4 at these sites is not significant. The cause of this may simply be the inter-annual noise in the meteorology obtaining a small signal. However, this raises the question of stationarity, i.e. are all other conditions remaining constant during the 12 years of monitoring? The first and most obvious indicator is precipitation amount, which shows considerable inter-year variability but no monotonic trend. The relative frequency of winds, which transport pollutants from the source areas in the UK and other countries of Europe to remote regions of the UK, has been examined in earlier analyses of UK acid deposition (RGAR 1990, 1997). More recently the North Atlantic Oscillation (NAO) has been recognised as an important influence on European climate (Hurrell, 1995) and is discussed at length in later sections of this report. The NAO provides an index of ‘westerlyness’ in the airflow over the UK. Large Index (NAOI) values (or large pressure gradients) are associated with strong southwesterly airflow and a succession of fronts and precipitation over the UK. If marked changes of the NAOI occur during the 12 years of the available wet deposition data for the UK, then it may be argued that this would introduce additional variability into the precipitation chemistry measurement and mask trends. The annual NAO values plotted in Figure 2.9 show a clear maximum in NAO in the years 1990, 1992 with smaller positive value in 1986, 1989, 1991 and 1994, while 1987, 1988, 1995, 1996 and 1997 all show negative values (reduced westerlyness). A simple correlation of Cl^- concentration against NAO, using annual data reveals relatively little structure with the exception that the largest positive value is associated with the largest mean Cl^- concentration. Thus, the precipitation chemistry data at annual scales, as used for the deposition maps, show a weak association between these two variables.

The annual Cl^- deposition however, is highly episodic, with a substantial fraction of the deposition contributed by a few rainfall events each year. The data from the UK primary precipitation chemistry sites, which provide daily collection, show that all sites in the primary network are highly episodic in Cl^- deposition (defined as sites receiving >30% of the wet deposition in < 5% of the precipitation events). Furthermore, the Cl^- deposition is largely a winter phenomenon, with 80% of the deposition in the winter months.

The implication from this rather simplistic analysis is that inter-year variability in the weather has to some extent masked the SO_4^{2-} declines at the remote sites in the north and west of the country. The changes in the ‘westerlyness’, which are evident in the NAO data, and the associated changes in sea-salt deposition clearly introduce noise into the dataset. However, if the large decline in wet deposition and dry deposition observed at the sites in the source areas of the UK (~50%) was also present at these remote sites, such a signal would have been detected. The application of NAO indices for the winter months, as applied later in this report is consistent with the winter dominated deposition of sea-salts. Since a large fraction of the ionic content of precipitation at the west coast sites is provided by sea-salts, it is unsurprising that temporal variations in sea-salt deposition are strongly correlated with surface water chemistry. However, in this chapter we are specifically examining the available data to show whether the large reductions in sulphur emissions are evident in the deposition data and how the evidence varies throughout the country. The conclusion from the analysis is that large reductions in sulphur deposition during the last decade are evident, but that in many west coast areas of the country, the decline in sulphur deposition is very small, and is much smaller than the reduction in UK or European sulphur emissions. In conclusion, the lack of detection of a significant decline in sulphur deposition at some of these remote sites has probably been influenced by variations in the weather over the monitoring period. It is probable therefore that with continued reductions in emission the declining deposition will become clear even at these remote locations.

Figure 2.9

The changes with time in the annual North Atlantic Oscillation Index (NAOI)



2.6 Deposition trends at individual sites

Statistically significant trends are found at only 13 out of the 32 sites, these being the source region sites, Jenny Hurn, Driby, Bottesford, Stoke Ferry, Woburn, Flatford Hills, Compton and High Muffles, and the intermediate sites, Barcombe Mills, Wardlow Hay Cop, Eskdalemuir, Whiteadder, and Achanarras, the east coast site in northern Scotland.

However, all sites with the exception of Yarner Wood show negative trend, and by grouping the sites using a hierarchical clustering method into the four groups shown in Table 2.1 and Figure 2.3 the trends may be broadly classified on a regional basis. The trends may be shown to be significant for all groups when the data are considered together. This is the case even at the remote and west coast sites, (groups 3 and 4) where the slope of the decrease is 0.5 μeq SO_4^{2-} l^{-1} yr^{-1} and is statistically significant. The intermediate sites (group 2) show a trend of 1 μeq SO_4^{2-} l^{-1} yr^{-1}, while the source area (group 1) sites show the clear decreasing trend of 3 μeq SO_4^{2-} l^{-1} yr^{-1} (Figure 2.10). These broad classifications seem entirely appropriate to identify the region specific trends in non-marine SO_4^{2-} deposition and show that the magnitude of the trend at these remote sites is small. If, for example, we examine the trends at the nearest acid deposition network secondary collector to the appropriate UKAWMN site, then with the exception of Barcombe Mills, all trends are non-significant. With these small changes in precipitation chemistry at the remote sites, it would hardly be surprising if site specific surface water chemistry, which is further modified by interactions within the catchment, shows no trends.

For sites at the west coast with mean non-marine SO_4^{2-} concentrations of 20 μeq l^{-1}, a reduction by 10 μeq l^{-1} would have been readily detected over the 12 years of data available. The tabulated statistics in Appendix 1, Tables 1-4 refer to the 12 years of precipitation chemistry monitoring.

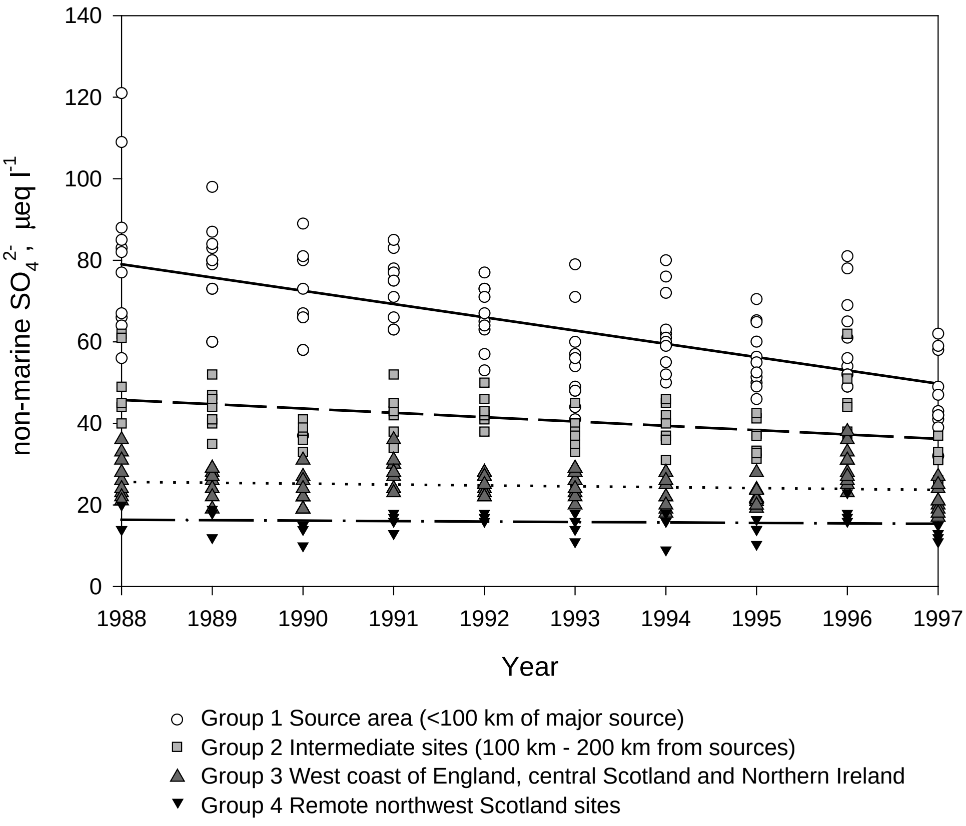


Figure 2.10

The linear trends in annual non-marine SO_4^{2-} in precipitation for four groups of sites in the UK acid deposition monitoring network. See Figure 2.3 for geographical distribution

To provide a strictly comparable set of data for comparison of the wet deposition and UKAWMN site data, the trend analysis has also been completed for the shorter (10 year) period of precipitation chemistry data of 1988 to 1997.

Considering these in turn.

Non-marine SO_4^{2-} trends (1988-1997)

(Appendix 1, Table 5)

The significant trends in SO_4^{2-} are the source area (1) and intermediate sites (2) (as with Figure 2.3) with slopes of the decline of 3 - 5 µeq SO_4^{2-} l^{-1} yr^{-1} and 1 µeq SO_4^{2-} l^{-1} yr^{-1} for the source regions and intermediate sites respectively. The remote regions consistently show a general decline but with the inter-year variability the trends are not statistically significant. The analysis of the shorter period is therefore entirely consistent with that for the 12 years.

NH_4^+ trends (1988-1997)

(Appendix 1, Table 6)

There are no consistent significant trends at the regional scale, and an even split of non-significant trends among the individual site data. While there is no evidence of a trend overall it is noticeable that in the source areas, the tendency is for a decline (Stoke Ferry, Bottesford, Jenny Hurn, Thorganby, High Muffles, Wodburn, Flatford Mills) but little can be drawn from such weak signals. Ammonia emissions are believed to have changed little over the monitoring period, but with such large changes in sulphur emissions, it is probable that changes in the aerosol chemistry have occurred, with a replacement of the ammonium sulphate by ammonium nitrate.

Cl^- trends (1988-1997)

(Appendix 1, Table 7)

The clear negative trends in Cl^- at the source area sites Bottesford, Jenny Hurn and Thorganby are entirely consistent with the decline in HCl emissions from the coal burning power-stations in the east Midlands and Yorkshire. It is surprising that the signal is not observed at High Muffles.

H^+ trends (1988-1997)

(Appendix 1, Table 8)

While H^+ has not been considered in detail in this chapter, these data merit a comment. It is notable that rainfall acidity has declined at all sites in the network over this period. The trends are significant at 16 sites and in the source areas the slope of the trend is fairly consistent at about 3 µeq H^+ l^{-1} yr^{-1} while at the intermediate and even some remote sites the trend is close to 1 µeq H^+ l^{-1} yr^{-1}. These declines are almost identical to the decline in SO_4^{2-} and in the absence of trends in NH_4^+ and NO_3^- imply that the acidity was SO_4^{2-} related. The sites not showing a significant trend are in general the west coast sites where the magnitude of the trend is < 1 µeq H^+ l^{-1} yr^{-1} and, like SO_4^{2-} at these sites, such signals are masked by the inter-year variability.

NO_3^- trends (1988-1997)

(Appendix 1, Table 9)

Unlike SO_2, the emissions of NO_x have not changed greatly during the period 1986 to 1997 (Figure 2.2). There was a gradual increase from 1986 to 1990 and since then NO_x emissions have declined steadily. These trends are somewhat smaller than those of other European countries, but overall the decline is small over the period (EMEP, 1999). The observed UK precipitation chemistry shows a small but significant increase in NO_3^- concentration at many of the remote west coast sites (Yarner Wood, Llyn Brianne, Pumluman, Bannisdale, Lough Navar and also at Eskdalemuir. The magnitude of the change seems small at about 0.5 µeq NO_3^- l^{-1} $year^{-1}$. However, the weighted mean concentration at these sites in the early years of the measurement were very small, 8 - 15 µeq NO_3^- l^{-1} and the increase represents a 20% increase in wet deposition at many of the sites. The cause of the trend is unknown, and in the absence of any measurement artefact implies an increase in aerosol NO_3^- and/or HNO_3 at these remote locations during this period. Only one site in the network (Bottesford) showed a significant decrease in NO_3^-.

The remote sites, most appropriate for the AWMN show no monotonic trends in the concentrations of any other major ion in precipitation, but considerable inter-year variability. Thus there is no evidence of other country-wide changes in major ions. A decrease in non-marine Cl^- has been observed at the east Midlands and Yorkshire sites, consistent with reduced emissions of HCl from coal combustion in these areas.

2.7 Summary

- UK and non-UK European S emissions both declined between 1986 and 1997 by approximately 55%. UK NO_x emission declined by 14% during the same period.

- Sulphur deposition in the UK declined by approximately 50% between 1986 and 1997, but the majority of the decline was dry deposition (61%), the decline in wet deposition was 42%.

- Concentrations of non-marine SO_4^{2-} and H^+ in precipitation over the period 1986-1997 and 1988 to 1997 both declined at: 3 $\mu eq\ l^{-1}\ yr^{-1}$ at sites close to (<100 km) major sources (the east Midlands of England and Yorkshire) : 1 $\mu eq\ l^{-1}\ yr^{-1}$ at sites 100 km to 300 km from sources. At the remote high rainfall west coast locations in Britain the decline in SO_4^{2-} concentration was barely detectable.

- There were large year to year variations but no monotonic trends in precipitation amount during the period of measurement.

- The North Atlantic Oscillation (NAO) Index showed a pronounced positive peak in the early 1990s and large sea-salt concentrations in rain during the peak and troughs in the late 1980s and mid 1990s. This cyclical change in the 'westerlyness' of the climate introduced variability which may have obscured the signal of SO_4^{2-} concentration and S deposition reductions at the high rainfall west coast sites.

- Very clear large reductions in both wet and dry deposition of S in the source regions of the UK and at intermediate distances from the source areas (see Figure 2.3 and Table 2.1) are evident in the measurements. There are reductions in S deposition in the high rainfall, west coast areas but the reductions are much smaller than the reductions in UK or non-UK European S emissions and at many of the high rainfall sites the trends in deposition are not statistically significant. The observed changes in precipitation chemistry measured by the UK deposition network are consistent with observed surface water chemistry measurements by the UKAWMN network.

- Small but significant increases in concentrations and deposition of NO_3^- are evident at the west coast and remote monitoring stations.