

ATMOSPHERIC DEPOSITION AT ROTHAMSTED, SAXMUNDHAM, AND WOBURN EXPERIMENTAL STATIONS, ENGLAND, 1969–1984

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Abstract. The pH of precipitation, and the concentrations in precipitation and depositions by precipitation of H^+ , major cations, N, S, and chloride were measured in bulk collectors at three sites in Eastern England. The Rothamsted site is 100 km from the coast in a semi-urban environment. The Saxmundham site is 13 km and the Woburn site 120 km from the coast; both are in rural environments. Precipitation is acidic at all three sites, with a pH of 4.3 at Rothamsted and 5.0 at Saxmundham and Woburn at present, but the pH has been increasing. Precipitation chemistry is chiefly controlled by sea-salts (Na, Mg, Cl) and earth salts (K, Ca, Mg, NH_4 , NO_3). Sea-salts dominate near the coast at Saxmundham, but earth salts become much more important inland at Rothamsted and at Woburn. The concentration and deposition of non-sea Cl are increasing at Rothamsted and Saxmundham, those of non-sea SO_4 -S are increasing at Woburn, and those of NO_3 -N are increasing at all of the sites. Precipitation acidity is associated chiefly with non-sea SO_4 , and only a little with NO_3 and non-sea Cl, at Rothamsted and Woburn. At Saxmundham, no correlation between acidity and anions is observed, presumably because of the overwhelming effect of sea-salts.

1. Introduction

Lawes and Gilbert began analyzing precipitation at Rothamsted Experimental Station, Hertfordshire, England, in 1853, and analyses have continued periodically ever since. Lawes *et al.* (1882), Miller (1905), and Russell and Richards (1919) reported early data, and Brimblecombe and Pitman (1980) summarized all data up to 1977. Williams began the most recent study in 1969 and included two other experimental sites: Woburn Experimental Farm, Bedfordshire, and Harwood's Field, Saxmundham, Suffolk. The result of the first 5 yr of this study were reported by Williams (1976). He initiated the work because of rising concern over the pollution of groundwaters by agricultural fertilizers, especially nitrates and phosphates. Recently, there has been much concern over the effect of the deposition of acidifying ions from the atmosphere, particularly S and N from anthropogenic sources, the so-called Acid Rain. Much work has been carried out in the last 10 to 15 yr, measuring acid deposition and looking at causes and effects. Several major conferences have been held to discuss findings (e.g., Hutchinson and Havas, 1980; Drablos and Tollan, 1980; Martin, 1982; Swedish Ministry of Agriculture, 1982; Teasley, 1982; Pierce *et al.*, 1983) and reports written on the subject (e.g., Environmental Resources Limited, 1983; Fry and Cooke, 1984; Buckley-Golder, 1984). Barrett *et al.* (1983) published a survey of the distribution of acid deposition in

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the U.K. Unfortunately, much of the country including some of the most important arable land in the East of England was omitted. Our data on atmospheric deposition at three sites in this part of the country fills one of the gaps and gives some indication of sources of acidity. Also, the Rothamsted data, the longest record of acid deposition in the world, allow short-and long-term trends to be examined.

2. Experimental

2.1. SAMPLING SITES

The locations of the three sampling sites are shown in Figure 1. They are at altitudes of 128 m (Rothamsted), 37 m (Saxmundham), and 89 m (Woburn). Rothamsted is in a semi-urban environment on the western edge of the town of Harpenden (population 30 000), 25 km NW of London. Woburn Experimental Farm is in a rural setting 3 km N of Woburn Abbey and 50 km NW of London. Harwood's Field is also in a rural situation, 2 km W of the town of Saxmundham and 130 km NE of London. All three sites are in areas of predominantly arable farming. Saxmundham is about 13 km from the east coast of England, and so its atmospheric deposition would be expected to be strongly influenced by the sea. Rothamsted is approximately 100 km and Woburn 120 km from the coast.

2.2. SAMPLING METHODS

At each site, precipitation is collected in a 14 cm diameter polythene funnel placed in a 1 L polythene bottle. This assembly is fixed 1.2 m above ground in a meteorological enclosure. Samples are collected twice monthly at Rothamsted, and approximately monthly at Saxmundham and Woburn. The collectors are of the very simple type used to estimate 'bulk' deposition – wet, dry, and occult (mist and fog) (Barrett *et al.*, 1983). Algicide is added to prevent algal growth, and samples are filtered where necessary to remove insects and other debris. Precipitation volume collected in the bulk gauges is recorded, and the samples stored at 5 °C until analyzed.

Samples are analyzed for Na, K, Ca, and Mg by atomic absorption. $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, $\text{PO}_4\text{-P}$, and Cl are analyzed absorptiometrically and $\text{SO}_4\text{-S}$ turbidimetrically using a Technicon Auto-analyzer; detection limits for the latter group are 0.05, 0.01, 0.05, 0.5, and 0.1 mg l^{-1} , respectively. Williams (1971) gave full details of the methods used. $\text{PO}_4\text{-P}$ is almost always undetectable and so is not reported.

The collectors consist of an open funnel, and so contamination from bird droppings, insects, and other organic debris sometimes occurs. Lewin and Torp (1982) found that such contamination greatly increased pH and $\text{NH}_4\text{-N}$ concentration, but did not affect Cl^- , $\text{NO}_3\text{-N}$, and $\text{SO}_4\text{-S}$ concentrations. In accordance with this, we took samples to be contaminated if they had an anomalously high pH (> 6) and $\text{NH}_4\text{-N}$ concentration (> 10 mg L^{-1}). Such samples comprised approximately 4% of the total and were omitted. This of necessity affects the mean pH and concentration of $\text{NH}_4\text{-N}$, but not any other ions.

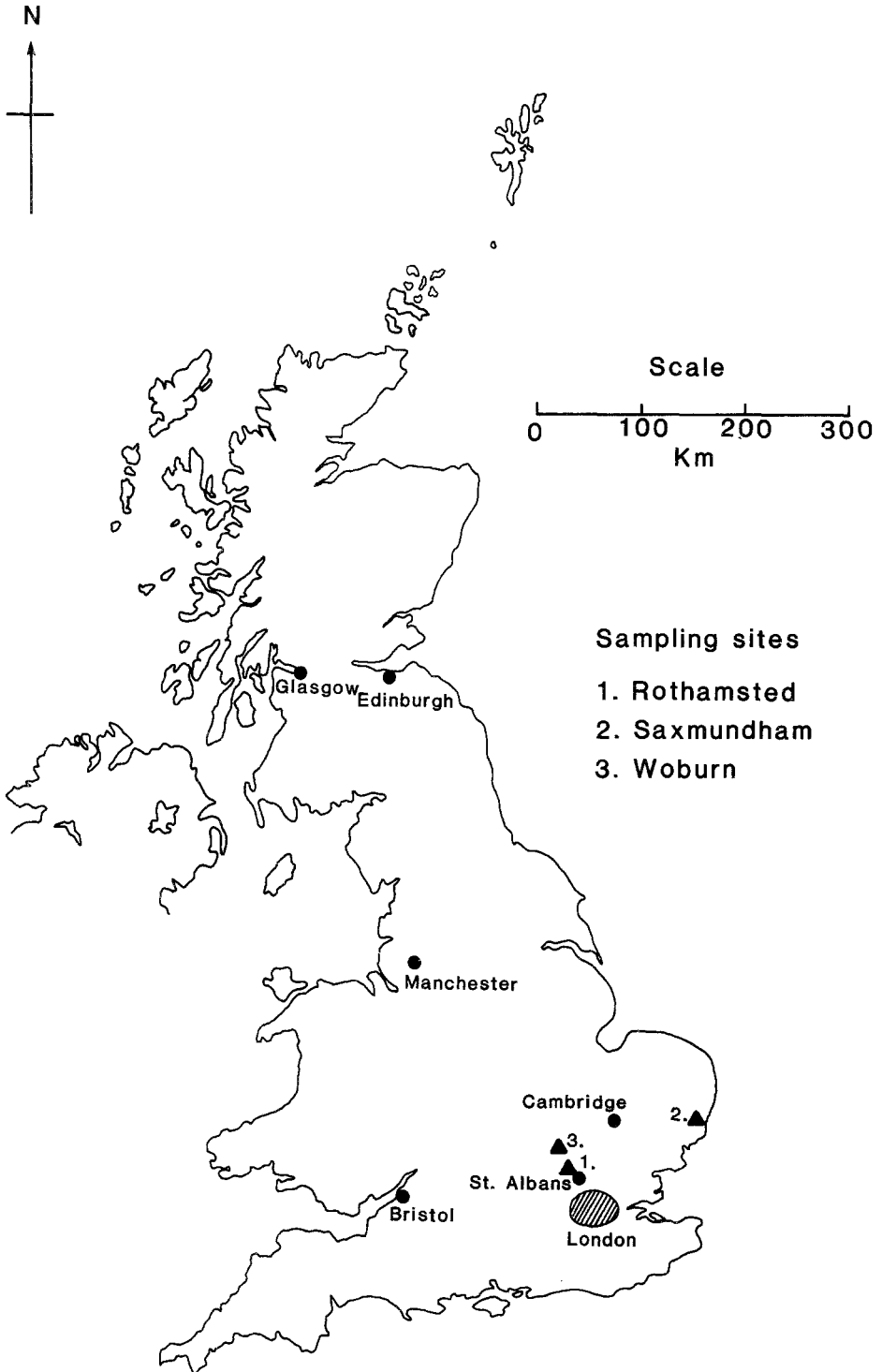


Fig. 1. Location of the sampling sites.

For each year the annual mean and standard deviation of the precipitation weighted monthly or twice-monthly values of pH and ionic concentration were calculated. These enable trends during the 16 yr study period to be established. Precipitation weighted monthly means and standard deviations were also calculated for the entire period to show seasonal trends. Annual depositions were calculated from annual means and annual precipitation measured in a standard 5 in. rain gauge.

We present data for the years 1969–1984, with the exceptions that (a) cations were not measured from 1982–1984; and (b) pH was not measured in 1982 at Rothamsted or at Woburn.

For the years 1982–1984 precipitation volume collected in the bulk gauges was not recorded. It was obtained from daily readings of the adjacent standard 5 in. rain gauge, there being a linear relationship between the precipitation collected in the two gauges.

We have used linear regression analyses to examine trends. Only those in which the slopes of the trendlines are significantly different from zero are discussed.

The data presented here differ slightly from those in a recent paper which summarized N, S, and Cl deposition and precipitation acidity from 1969 to 1983 at the same sites (Goulding and Poulton, 1985). This is because Goulding and Poulton's data was not weighted for precipitation volume, and because of the extra years' data (1984) included here.

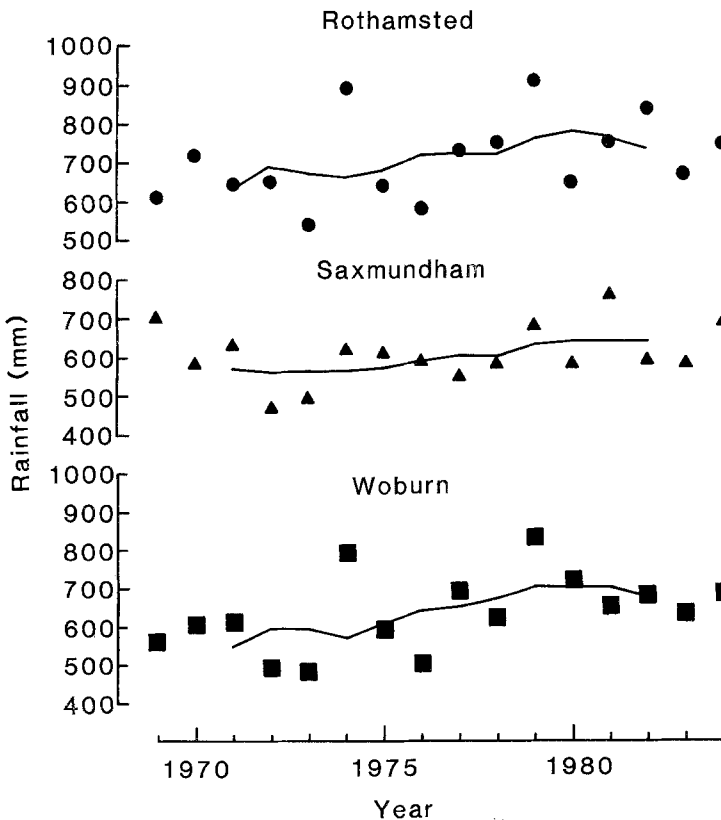


Fig. 2. Trends in precipitation volume from 1969–1984.

3. Results

3.1. PRECIPITATION

Trends in annual precipitation, collected in a standard 5 in. rain gauge at the sites are shown in Figure 2, with lines joining 5 yr running averages to show these trends more clearly. The mean annual precipitation values for the whole 16 yr period are: Rothamsted, 705 mm; Saxmundham, 606 mm; and Woburn, 633 mm. Although there is much variation, especially inland at Rothamsted and Woburn, linear regression analysis shows that precipitation has been increasing significantly at these two sites: by 8.7 mm yr^{-1} at Rothamsted and 9.6 mm yr^{-1} at Woburn. The amounts of dissolved material deposited depend on precipitation as well as on concentration, and so any increases in deposition at Rothamsted and Woburn over the 16 yr period will be due at least in part, to the increase in precipitation.

3.2. ACIDITY

Trends in the pH of precipitation are shown in Figure 3. Mean pH values over the study period were 4.4 at Rothamsted, 4.8 at Saxmundham, and 4.7 at Woburn, but the fluctuations apparent in Figure 3 show that such medium-term means should be

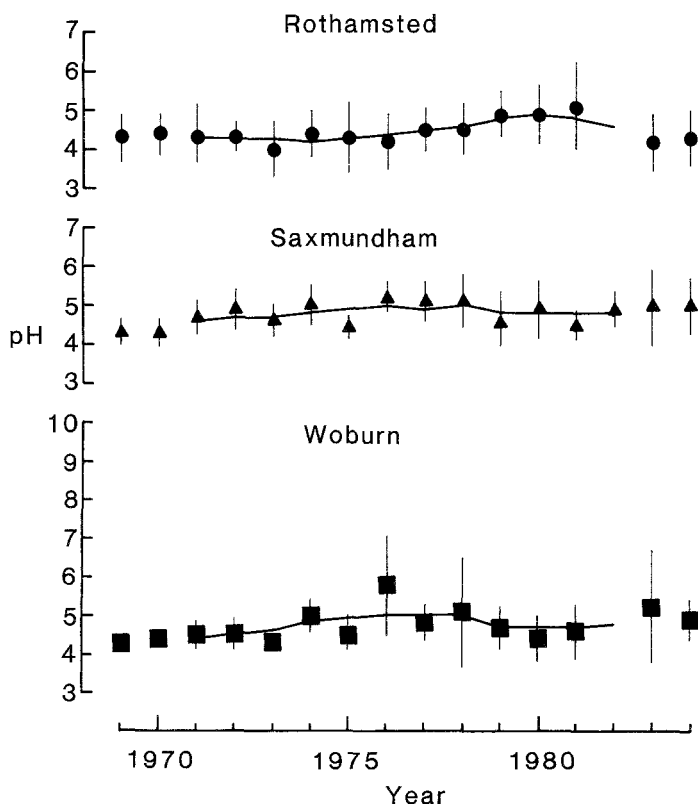


Fig. 3. Trends in the pH of precipitation from 1969-1984.

interpreted with care. Present pH values are approximately 4.3 at Rothamsted, and 5.0 Saxmundham and at Woburn. Precipitation has become slightly less acid over the period of study, increasing by 0.025 ± 0.016 , 0.030 ± 0.015 , and 0.038 ± 0.021 units per annum at Rothamsted, Saxmundham and Woburn, respectively. The slight increase in acidity at Rothamsted from 1969–1977 reported by Brimblecombe and Pitman (1980) has been outweighed by a rather greater decrease from about 1976 to 1981, but acidity is now increasing again. At this site, therefore, precipitation pH has exhibited a cyclical change rather than a smooth trend (Figure 3). The overall decrease in acidity opposes the trend that some other investigators (e.g., Martin, 1979) have reported. Unfortunately the recent report on Acid Deposition in the U.K. (Barrett *et al.*, 1983) found a paucity of reliable data to indicate trends in acidity. The report suggested some increase over 'recent years', but this appears to relate precipitation pH of the last 10 yr with that in the 1930s and 1950s. Our data suggest that after increasing through the 1960s and 1970s, acidity may now be decreasing at least in some areas (see also Section 4.3 below).

The very high pH of precipitation at Woburn in 1976 coincided with a very hot, dry summer. Generally, seasonal variation of pH (Figure 4) shows autumn maximum at Rothamsted, a late summer/early autumn maximum at Saxmundham, but summer and winter maxima at Woburn. Variation generally increases with pH, i.e., the standard deviation of the annual and monthly mean pH increased as the mean pH increased. We

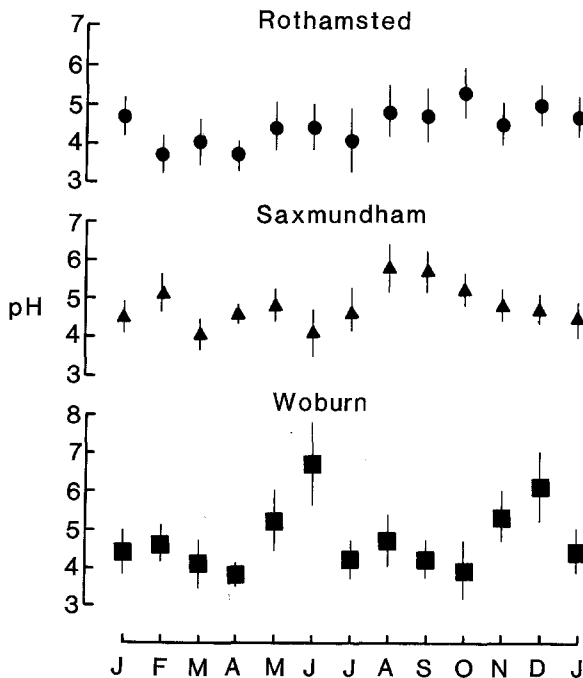


Fig. 4. Seasonal variation in the pH of precipitation, means of the years 1969–1984.

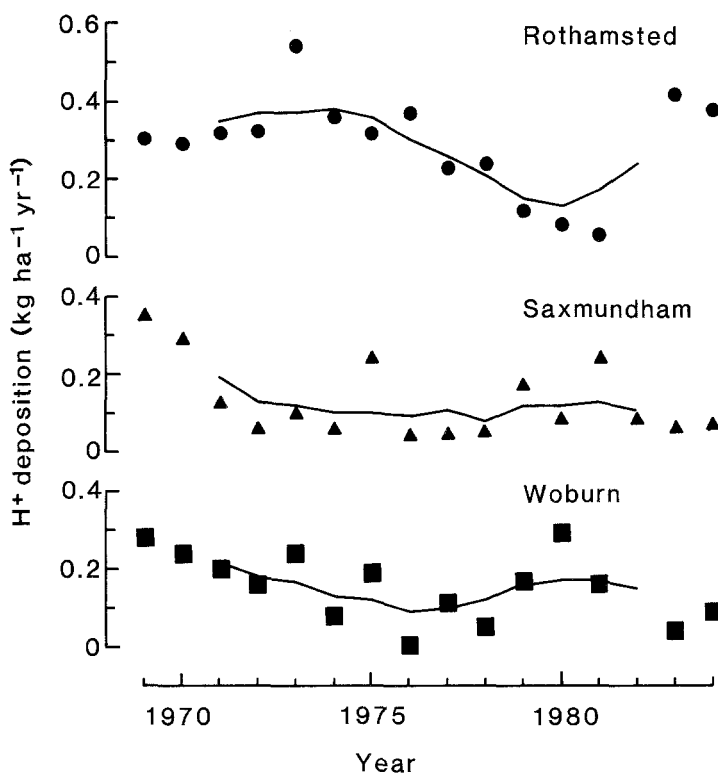


Fig. 5. Trends in the deposition of H^+ ($\text{kg ha}^{-1} \text{yr}^{-1}$) from 1969–1984.

attribute these observations to a very variable increase in dry deposition, especially of soil dust, in summer, which neutralizes some of the acidity (Lewin and Torp, 1982).

Little H^+ is deposited directly (Figure 5): present depositions are about $0.40 \text{ kg ha}^{-1} \text{yr}^{-1}$ at Rothamsted, and $0.10 \text{ kg ha}^{-1} \text{yr}^{-1}$ at Saxmundham and at Woburn. Trends in pH (Figure 3) are confounded by those in precipitation (Figure 2), so that Rothamsted shows an increase in deposition from 1969 to about 1976, followed by a sharp decrease until about 1981 and then a rapid increase again. Saxmundham and Woburn also show fluctuations but exactly the reverse of those at Rothamsted and more gradual.

3.3. MAJOR CATIONS

The concentrations of Na, K, Ca, and Mg in precipitation, seasonal changes in these concentrations, and trends in amounts deposited over the 16 yr period are shown in Figures 6, 7, and 8, respectively.

3.3.1. Sodium

Concentrations of Na in precipitation at Saxmundham ($\approx 5 \text{ mg L}^{-1}$) are about 2.5 times those at Rothamsted and Woburn ($\approx 2 \text{ mg L}^{-1}$), and are much more variable,

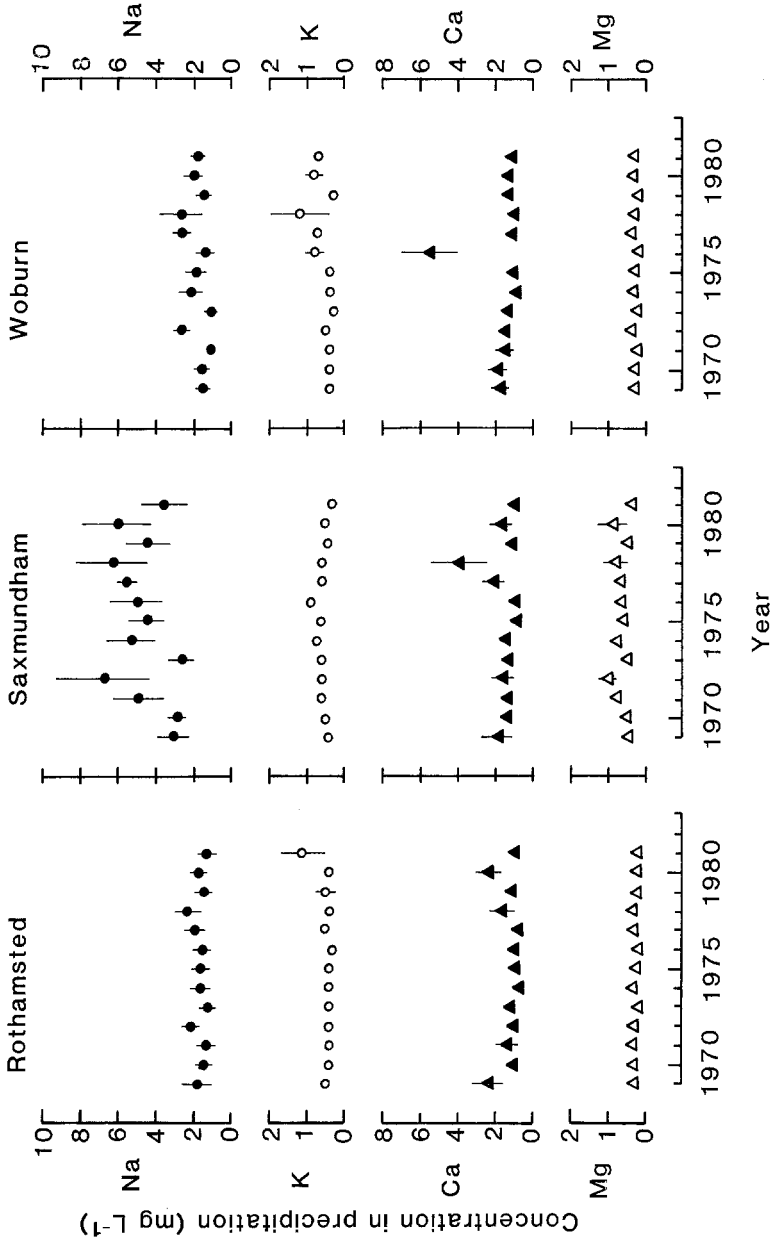


Fig. 6. Trends in the concentrations (mg L^{-1}) of major cations in precipitation over the years 1969–1981.

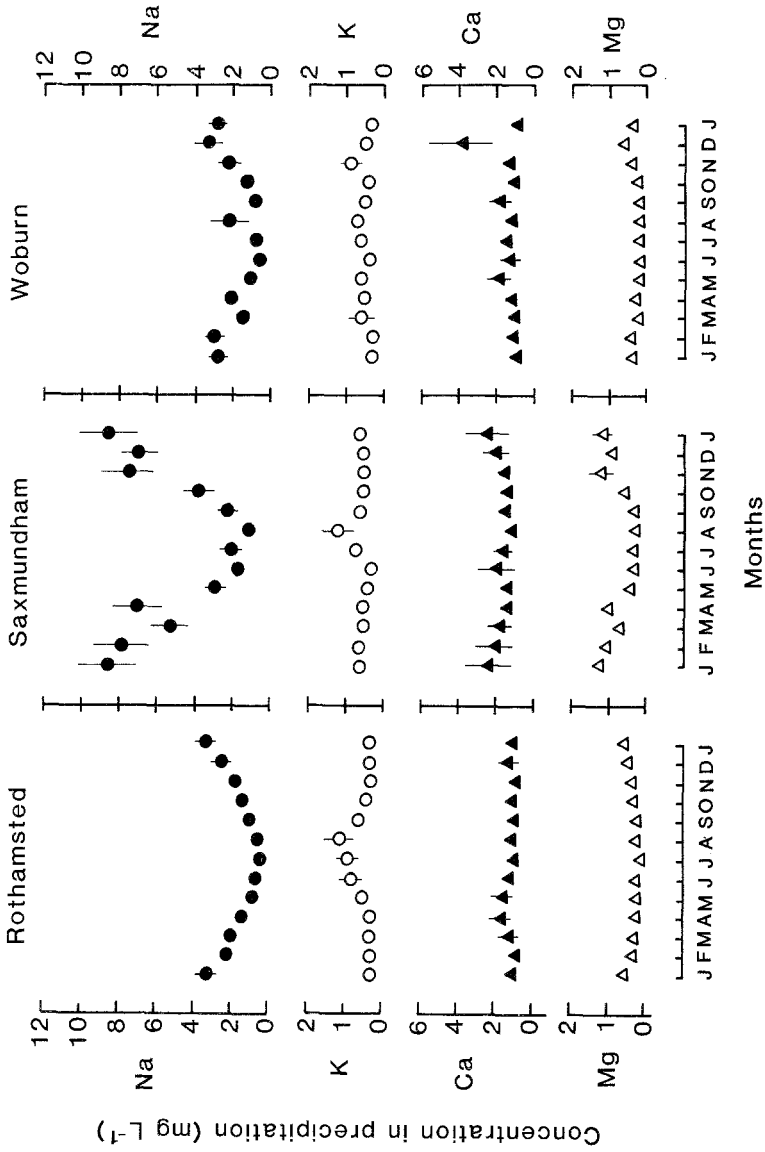


Fig. 7. Seasonal variation in the concentrations (mg L^{-1}) of major cations in precipitation, means of the years 1969–1981.

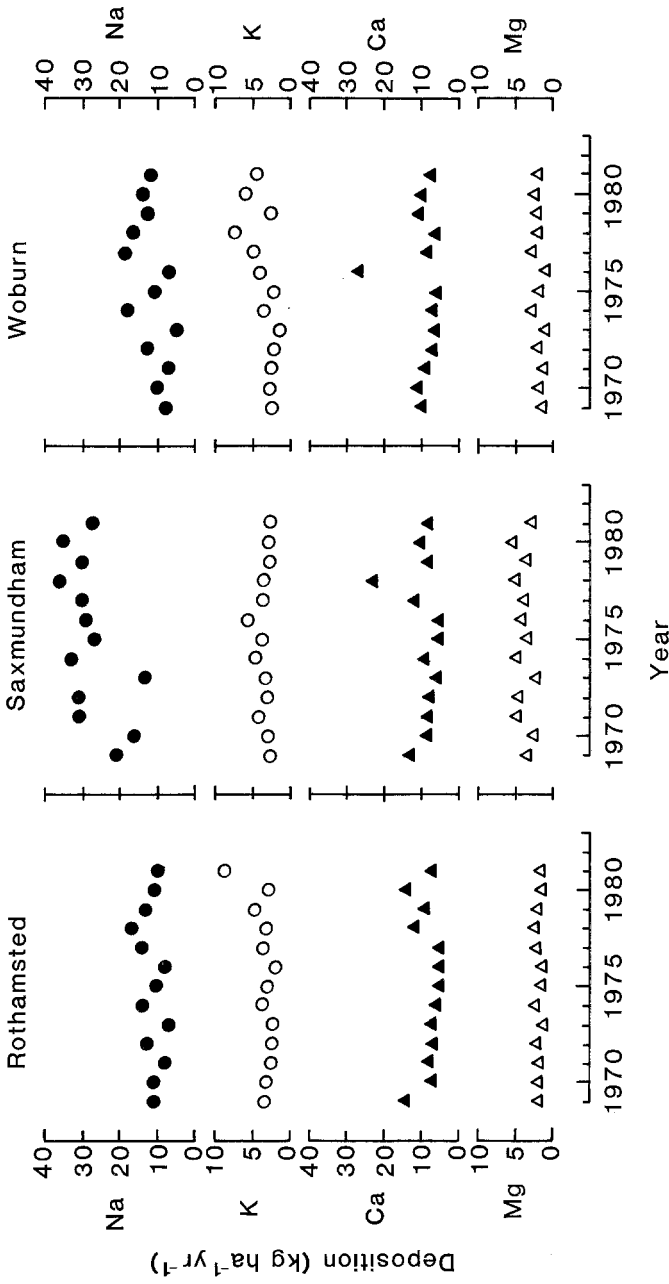


Fig. 8. Trends in the deposition ($\text{kg ha}^{-1} \text{yr}^{-1}$) of major cations over the years 1969–1981.

because of its proximity to the sea. Sodium and Cl concentrations are closely correlated at all three sites, especially at Saxmundham. Concentrations of Na are increasing at Saxmundham. Wind speed has increased slightly but significantly since 1969 and so more marine salts may have been picked up and carried further. Concentrations, and variation in concentrations, show a very smooth seasonal cycle, with pronounced winter maxima at all sites, especially at Saxmundham (Figure 7). Amounts of Na deposited (Figure 8), at present about 10 to 15 kg ha⁻¹ yr⁻¹ at Rothamsted and Woburn, 25 to 35 kg ha⁻¹ yr⁻¹ at Saxmundham, are increasing at each site because of the increase in concentration at Saxmundham, but only because of the increase in precipitation at Rothamsted and Woburn.

3.3.2. Potassium

Concentrations of K in precipitation (Figure 6) are small and about the same for each site (0.5–1.0 mg L⁻¹). They have been slightly increasing inland at Rothamsted and Woburn. There is a summer maximum, most pronounced at Rothamsted, suggesting that the main source of K is wind-blown soil particles. Amounts deposited at present are approximately 5 kg ha⁻¹ yr⁻¹ at Rothamsted and Woburn, and 3 kg ha⁻¹ yr⁻¹ at Saxmundham. They are increasing at Rothamsted and Woburn because of the increases in concentration and in precipitation.

3.3.3. Calcium

Calcium concentrations at all three sites have much the same mean of 1 to 2 mg L⁻¹ (Figure 6). No trends are apparent during the period of study. Amounts deposited are currently about 10 kg ha⁻¹ yr⁻¹. The very large concentration of Ca and amount deposited at Woburn in 1976 coincide with the anomalously high pH and hot dry summer. The same effect is seen, but to a smaller extent, at Saxmundham in 1977–1978.

3.3.4. Magnesium

Concentrations of Mg in precipitation (Figure 6) are very small and constant. Those at Saxmundham (ca. 0.7 mg L⁻¹) are about twice those at Rothamsted and Woburn (ca. 0.3 mg L⁻¹), because almost all of its Mg comes from the sea. This interpretation is supported by the close correlation (Variance Accounted For, VAF = 73.9%, $p < 0.001$) of Mg with Cl at Saxmundham. It is also reflected in the seasonal trends (Figure 7), for which all of the sites show a winter maximum but which is barely noticeable inland. Much of the Mg at Rothamsted and Woburn must, therefore, come from soil dust. Deposition (Figure 8) is currently 2–3 kg ha⁻¹ yr⁻¹ inland, 3–5 kg ha⁻¹ yr⁻¹ at the coast.

3.4. NITROGEN, SULPHUR, AND CHLORIDE

Concentrations of NH₄-N, NO₃-N, SO₄-S, and Cl in precipitation seasonal trends in concentrations, and amounts deposited over the study period are shown in Figures 9, 10, and 11, respectively. Non-marine or 'excess' SO₄-S and Cl have been estimated from total Na, SO₄-S and Cl and bulk Na : SO₄ and Na : Cl ratios in sea water using

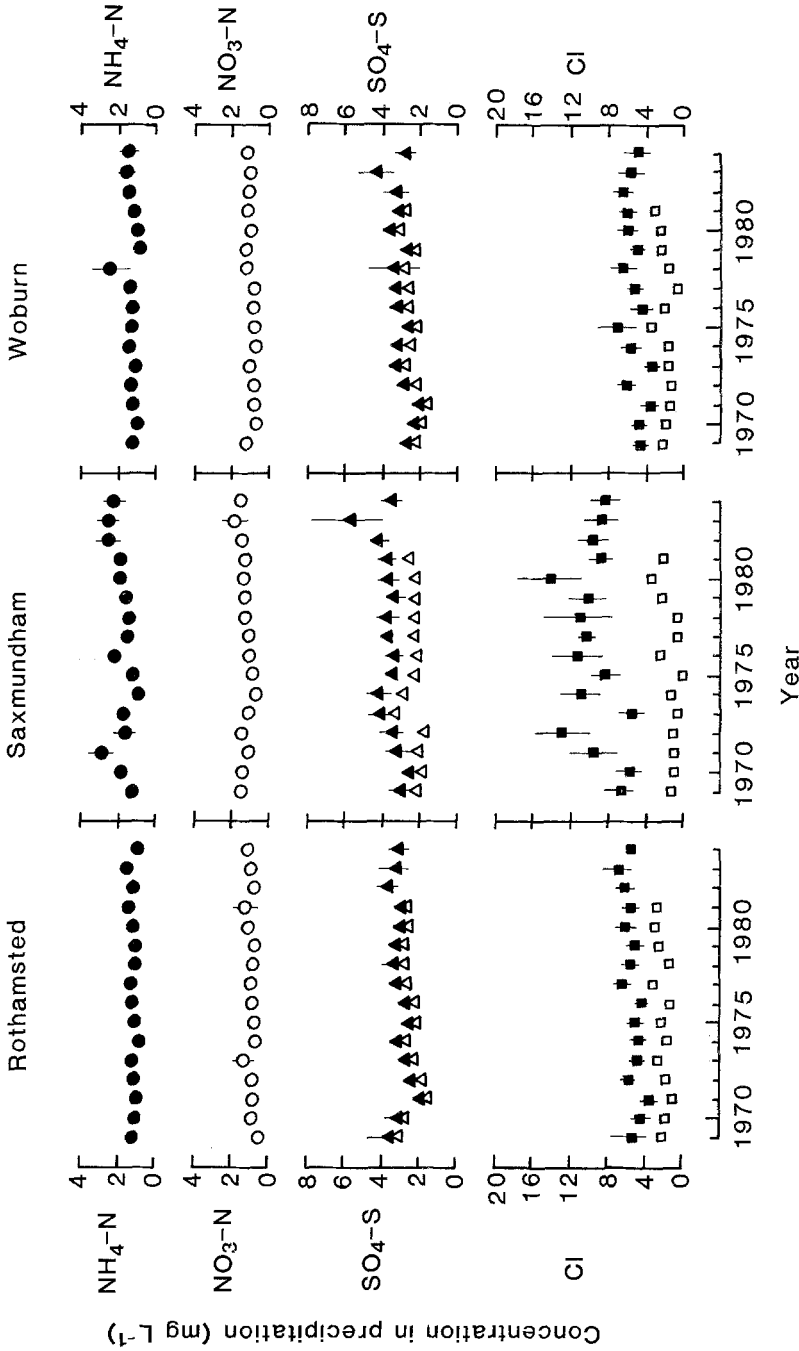


Fig. 9. Trends in the concentrations (mg L⁻¹) of N, S (▲ = total, △ = non-sea) and chloride (■ = total, □ = non-sea) in precipitation over the years 1969–1984.

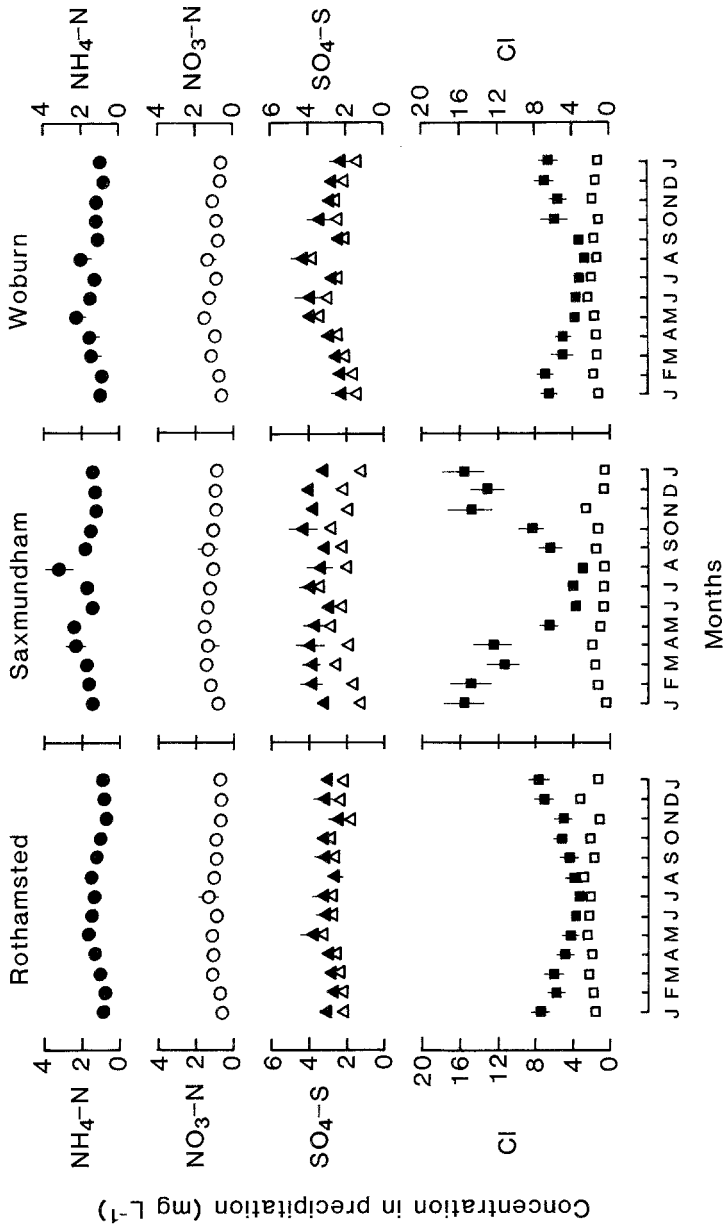


Fig. 10. Seasonal variation in the concentrations (mg L^{-1}) of N, S (\blacktriangle = total, \triangle = non-sea), and chloride (\blacksquare = total, \square = non-sea) in precipitation, means of the years 1969–1984.

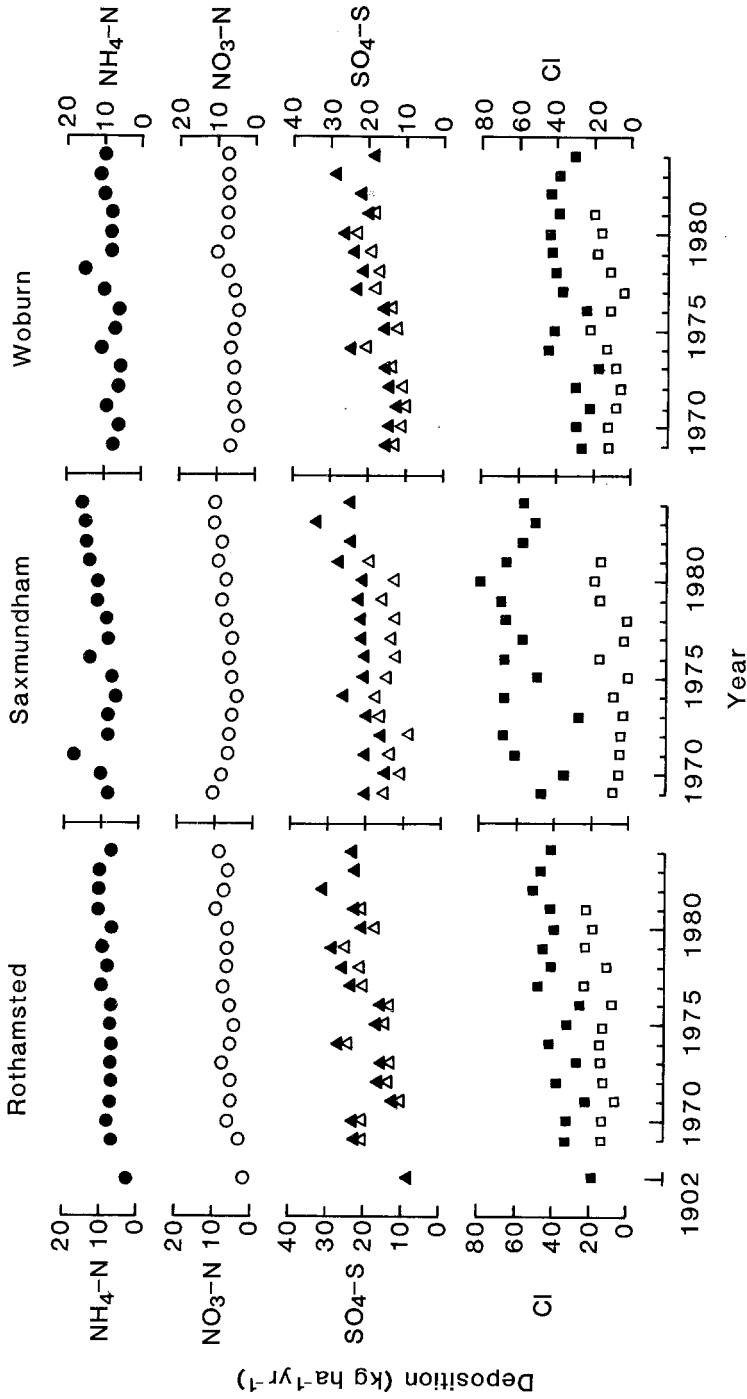


Fig. 11. Trends in the deposition ($\text{kg ha}^{-1}\text{yr}^{-1}$) of N, S (\blacktriangle = total, \triangle = non-sea), and chloride (\blacksquare = total, \square = non-sea) in precipitation over the years 1969-1984.

formulae given by Martin and Barber (1978):

$$\text{Non marine SO}_4\text{-S} = \text{total SO}_4\text{-S} - 0.25 \text{ Na} , \quad (1)$$

$$\text{Non marine Cl} = \text{total Cl} - 1.80 \text{ Na} . \quad (2)$$

3.4.1. Ammonium-N

Concentrations of $\text{NH}_4\text{-N}$ in precipitation are about 1 mg L^{-1} at Rothamsted, $1\text{--}2 \text{ mg L}^{-1}$ at Woburn, and $\approx 2 \text{ mg L}^{-1}$ and more variable at Saxmundham (Figure 9); they have been increasing slightly at Saxmundham and Woburn. They exhibit maxima in both spring *and* summer at all three sites (Figure 10). Variation of the mean concentration increases with concentration. Ammonia usually derives from agricultural sources (e.g., ammonium fertilizers, animal urine, ammonia volatilization from soil), with some from combustion. The seasonal maxima observed coincide with peak times for fertilizer application and ammonia volatilization.

Amounts deposited (Figure 11) are currently 5 to $10 \text{ kg ha}^{-1} \text{ yr}^{-1}$ at Rothamsted, $10 \text{ kg ha}^{-1} \text{ yr}^{-1}$ at Woburn and $15 \text{ kg ha}^{-1} \text{ yr}^{-1}$ at Saxmundham, compared with about $3 \text{ kg ha}^{-1} \text{ yr}^{-1}$ in the years 1888–1916 (Miller, 1905; Russell and Richards, 1919). Deposition has been increasing because of increases in precipitation at Rothamsted and at Woburn, and because of increases in concentration at Saxmundham and Woburn.

3.4.2. Nitrate N

Concentrations of $\text{NO}_3\text{-N}$ in precipitation are about 1 mg L^{-1} at each site (Figure 9). They have been increasing very slightly at all three sites. Concentrations exhibit a spring/early summer maximum (Figure 10) as others have found (Barrett *et al.*, 1983). Some 5 to 10 kg ha^{-1} of $\text{NO}_3\text{-N}$ are deposited each year (Figure 11), compared with about $1.5 \text{ kg ha}^{-1} \text{ yr}^{-1}$ from 1888–1916 (Miller, 1905; Russell and Richards, 1919). Deposition has been increasing because of the increases in concentration and because of the increases in precipitation at Rothamsted and at Woburn. Nitrate is thought to derive from combustion, especially vehicle exhausts, and from nitrification of NH_4^+ in soil (Martin, 1982). Spring maxima coincide with times when there is most nitrification. The increases in concentration and in amounts deposited over the period of study may be related to increases in application of nitrate fertilizers or to increased production of NO_x from the combustion of fossil fuels, especially vehicle exhausts (Barrett *et al.*, 1983).

3.4.3. Sulphate-S

Total concentrations of $\text{SO}_4\text{-S}$ in precipitation from marine and anthropogenic sources are at present about $3\text{--}4 \text{ mg L}^{-1}$ at Rothamsted and Woburn, and 4 mg L^{-1} at Saxmundham (Figure 9). They have been increasing markedly at all three sites, but at Rothamsted only since 1972. Seasonal changes (Figure 10) show little variation at

Rothamsted and Saxmundham, but a quite smooth yearly cycle with a summer maximum at Woburn. Barrett *et al.* (1983) observed a winter maximum for the deposition of SO₂ gas, but a spring maximum for SO₄²⁻ in precipitation. Total amounts of SO₄-S deposited, from 20 to 30 kg ha⁻¹ yr⁻¹, have been increasing markedly at all three sites (Figure 11). This is because of increases in concentration, and also increases in precipitation at Rothamsted and Woburn. The present figures compare with average amounts deposited at Rothamsted of 8 kg ha⁻¹ yr⁻¹ from 1881–1887 (Miller, 1905).

Non-marine SO₄-S arises, mostly from particulate S from aged SO₂ emissions (OECD, 1977). Inland, at Rothamsted and Woburn, concentrations (Figures 9 and 10) and therefore amounts deposited (Figure 11), comprise on average about 85% of total SO₄-S. Near the coast at Saxmundham the contribution of non-marine to total SO₄-S is about 70%. Seasonal trends (Figure 10) show a summer maximum in concentrations which is most pronounced at Woburn. This summer maximum is almost completely balanced by a winter maximum in marine SO₄-S at Rothamsted and Saxmundham to give virtually constant total concentrations. The data in Figures 9 and 11 show that it is the increases in non-marine SO₄-S that are causing the increases in total SO₄-S.

3.4.4. Chloride

Trends in concentrations of Cl in precipitation (Figure 9), in seasonal changes in those concentrations (Figure 10), and in amounts of Cl deposited (Figure 11) follow those of Na very closely. Calculations made using Equation (2) estimate that 85% of total Cl comes from the sea at Saxmundham, 60% at Rothamsted and Woburn. Concentrations of Cl in precipitation are currently 4 to 6 mg L⁻¹ at Rothamsted and Woburn, and 8 to 10 mg L⁻¹ and much more variable at Saxmundham (Figure 9). They have been increasing steadily at Rothamsted and Woburn. Figure 9 shows that these increases are caused primarily by increases in non-marine Cl (from gaseous HCl emitted during the combustion of fuels containing Cl (OECD, 1977)). There is a very smooth seasonal cycle of total Cl concentrations, wholly caused by changes in sea-derived Cl; concentrations of non-sea Cl remain almost constant throughout the year. This seasonal cycle is much more pronounced near the coast, as would be expected.

Deposition of total Cl at Rothamsted, measured from 1888–1916, was approximately 17 to 20 kg ha⁻¹ yr⁻¹ (Miller, 1905; Russell and Richards, 1919). Total amounts of Cl deposited are at present about 40 kg ha⁻¹ yr⁻¹ at Rothamsted and Woburn, and 50 to 60 kg ha⁻¹ yr⁻¹ at Saxmundham. They have been increasing quite quickly at the inland sites.

4. Discussion

4.1. ACID DEPOSITION IN EASTERN ENGLAND

The report by the U.K. Review Group on Acid Rain (Barrett *et al.*, 1983) gave important and useful data on acid deposition in the U.K. during the years 1978–1980. It showed maps of the concentrations and depositions of H⁺, non-marine SO₄-S, and NO₃-N

in rain, and data for some sites of $\text{NH}_4\text{-N}$. Unfortunately, because there were insufficient data, large parts of the U.K. were left blank on the maps, including much of the most important arable agricultural land in the East of England. Our data obtained using compatible methods of sampling and analysis allow this particular gap to be filled.

TABLE I

Comparison of precipitation-weighted mean pH, $\text{NH}_3\text{-N}$, $\text{NO}_3\text{-N}$, and non-sea $\text{SO}_4\text{-S}$ concentrations in precipitation at Rothamsted, Saxmundham, and Woburn for the years 1978–1980 with these quantities interpolated from the report of the U.K. Review Group on Acid Rain (Barrett *et al.*, 1983)

	Rothamsted	Saxmundham	Woburn	Barrett <i>et al.</i> (1983)
pH	4.8	4.9	4.7	4.2–4.4
$\text{NH}_4\text{-N}$ (mg L^{-1})	1.1	1.6	1.5	0.6–1.0
$\text{NO}_3\text{-N}$ (mg L^{-1})	0.8	1.2	1.1	0.5–0.8
Non-sea $\text{SO}_4\text{-S}$ (mg L^{-1})	2.6	2.2	2.7	1.1–1.7

Table I lists precipitation-weighted mean pH values and $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and non-marine $\text{SO}_4\text{-S}$ concentrations in precipitation at Rothamsted, Saxmundham, and Woburn for the years 1978–1980. It also includes estimated values for these sites, interpolated from the nearest sites in the Review Group's report which are, on average, 95 to 100 km from Rothamsted and Woburn, and 165 km from Saxmundham. Concentrations of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and especially $\text{SO}_4\text{-S}$ measured at our sites are larger than those interpolated from the report, suggesting that the atmosphere at our sites is a little more contaminated. The pH values at our sites are also higher, however, and our precipitation contains only one-third as much acid ($[\text{H}^+] \approx 16 \mu\text{eq L}^{-1}$) as that at the nearest sites in the report ($[\text{H}^+] \approx 50 \mu\text{eq L}^{-1}$). The sites chosen by Barrett *et al.* (1983) were selected as being rural and free from local influences. Our sites were not specially selected in this way because we are interested in the depositions they receive, not in determining an overall background level for rural sites. The local influences that may affect the atmosphere around our sites are discussed in Section 4.4.

4.2. IONIC BALANCES IN PRECIPITATION

Calculated ionic balances ($[\sum_{\text{Anions}} - \sum_{\text{Cations}}]/[\sum_{\text{Anions}} + \sum_{\text{Cations}}] \times 100\%$, Table II) show an anion excess in most years. Ionic balances should be within $\pm 10\%$ of the total anion and cation sum to be acceptable by National Association of Testing Authorities standards, but this limit may often be exceeded in waters of very low total ionic concentrations (Johnson *et al.*, 1979). While many British data have been found to be within the limit of acceptance (e.g., Cape *et al.*, 1984; Reynolds *et al.*, 1984), it is exceeded for about half of our data: 8 out of 13 yr at Rothamsted, and 5 out of 13 yr at Saxmundham and at Woburn.

In a previous paper (Goulding and Poulton, 1985) the anion excess was attributed to dry deposited SO_2 and NO_x . While considerable amounts of these gases are collected

TABLE II

Ionic balances, as $(\Sigma_{\text{Anions}} - \Sigma_{\text{Cations}})/(\Sigma_{\text{Anions}} + \Sigma_{\text{Cations}}) \times 100\%$, for Rothamsted, Saxmundham, and Woburn for the years 1969–1981 when full data were available

Year	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981
Site													
Rothamsted	6	17	0	7	11	21	13	9	22	12	26	14	22
Saxmundham	5	-1	-4	6	11	14	8	9	6	-2	15	11	16
Woburn	6	2	3	5	15	18	9	-10	9	8	25	20	20

(see Section 4.4 below) any oxidation to SO_4^{2-} and NO_3^- will also produce cations, usually H^+ . The anion excess cannot be attributed simply to inaccurate analyses, such as an overestimation of $\text{SO}_4\text{-S}$ or Cl , or erroneously high pH values. Examination of the data suggests different causes at each of the sites. At Rothamsted and Woburn there is a positive correlation of the anion excess with rainfall, $\text{VAF} = 53.9$ and 43.4% , respectively, $P < 0.01$. Perhaps at these sites, only 25 km apart, there are components in precipitation which are not subject to analysis. Paces (1985) found quite large amounts of Fe, Al, and Si in precipitation in forest and agricultural areas of Czechoslovakia, and Reid *et al.* (1981) found smaller amounts in precipitation in NE Scotland. Johnson *et al.* (1979) could attribute anion excess in the natural waters they studied to the presence of silicic acid or silica gel. It is possible that at our three sites silicates from soil dust are the main cause of the imbalance. There are also significant negative correlations of the anion excess with $[\text{H}^+]$ at Rothamsted ($\text{VAF} = 31.9\%$, $p < 0.05$) and with $[\text{Ca}^{2+}]$ at Woburn ($\text{VAF} = 37.6\%$, $p < 0.05$). It is most unlikely, however, that $[\text{H}^+]$ is underestimated at Rothamsted only, and $[\text{Ca}^{2+}]$ at Woburn only, because samples from all sites were analyzed together in the same laboratory. At Saxmundham, there are no significant correlations between the anion excess and other parameters, but here most ionic balances are within or near to $\pm 10\%$.

4.3. TRENDS IN ACID DEPOSITION

The problem of determining trends in acid deposition has recently been addressed in several research papers and reviews. Martin (1979) reported a general trend of increasing precipitation acidity (i.e., H^+) between 1928 and 1957, but that pH values had remained approximately constant since. Conversely, Brimblecombe and Pitman (1980), using Rothamsted data among others, reported that acidity had increased only since the late 1960s, but that $\text{SO}_4\text{-S}$ and $\text{NO}_3\text{-N}$ depositions had approximately doubled since the late 19th century. Assessing all the data available, the U.K. Review Group on Acid Rain (Barrett *et al.*, 1983) thought that changes of sampling site and methods of analysis made the detection of trends difficult, especially those in pH. However, they found that since the mid 19th century deposition of NO_3 had increased fourfold, doubling since 1900, and that recent increases in NO_3 deposition correlated closely with increases in production of NO_x from the combustion of fuel oils. They also found that SO_4 deposition had increased two-fold since the early 1930s, corresponding

to an increase in emission of SO_2 , but that SO_2 emissions had decreased since about 1970 because of fuel switching and an economic recession. Corresponding to this, Wharfe and James (1985) found a decrease in SO_2 concentrations in the atmosphere over N. Merseyside, England, since 1962 which has been accompanied by an increase in precipitation pH since at least 1978. Bristow and Garwood (1984) report a decrease in dry S deposition in a lysimeter experiment at the Grassland Research Institute, Hurley, Berkshire, from $40.6 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ in 1979 to $20.0 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ in 1982. Wet deposition did not change, however.

Do we see similar trends in our data? We must first distinguish between concentration and deposition. We have reported significant changes in the volume of precipitation over our 16 yr study period, and these (presumably short-term) changes strongly affect deposition. We do, though, see increasing deposition from increases in concentration of $\text{NO}_3\text{-N}$ at all the sites, non-marine $\text{SO}_4\text{-S}$ at Woburn, and non-marine Cl at Rothamsted and Saxmundham, with some evidence of recent decreases in Cl, but not $\text{SO}_4\text{-S}$ or NO_3 (Figure 9). By contrast there have been decreases in precipitation acidity and H^+ deposition at the sites. When we examine the data carefully, however, we see short-term increases and decreases in many of these long-term trends (see for example H^+ deposition in Figure 5, N, S, and Cl concentrations and especially depositions in Figures 9 and 11). It seems unwise, therefore, to place too much reliance on changes over a few years. Even if they are real, such changes may be explained by local influences, as suggested by Buckley-Golder (1984). We would agree with the U.K. Review Group on Acid Rain that at least 10 yr data are required to reveal trends clearly, and preferably much more than this. From the data of Wharfe and James (1985) and Bristow and Garwood (1984) it may be that a decrease in S emissions results initially in a decrease in dry rather than wet deposition. Unfortunately we have no recent data on dry deposition at our sites.

4.4. RELATIVE CONTRIBUTIONS OF WET AND DRY S DEPOSITION

Recent model estimates of wet and dry S deposition (Martin, 1980) have indicated a wet deposition of about $10 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ in the area around Saxmundham, $15 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ at Rothamsted and Woburn, and a dry deposition of about $15 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ at Saxmundham, 35 to $40 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ at Rothamsted and Woburn; the model is applicable to rural sites, away from towns and other local sources. The ratio of wet : dry deposition is thus 1 : 1.5 at Saxmundham, 1 : 2.5 at Rothamsted and Woburn. Bristow and Garwood's (1984) data confirm the model predictions for their site near Maidenhead, Berkshire, about 45 km from Rothamsted, but suggest that dry deposition there may have been decreasing markedly since the late 1970s. Comparing our data with the model suggests that our bulk gauges collect the wet plus all of the dry S deposited at Saxmundham, and the wet plus about 30% of the dry S deposited at Rothamsted and Woburn.

The model predictions differ somewhat from earlier Rothamsted data, however. Bromfield and Williams (1974) measured the dry deposition of S at Rothamsted by exposing samples of soil in Petri dishes in a Stevenson's screen. They obtained a figure

of $27.5 \text{ kg S ha}^{-1} \text{ yr}^{-1}$. They then separately calculated dry S deposition as the difference between 'wet' deposition in a 1/1000 acre rain gauge ($33.0 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) and S lost in drainage water from a 50 cm deep 1/1000 acre drain gauge on the same site ($58.4 \text{ kg S ha}^{-1} \text{ yr}^{-1}$), thus obtaining a value of $25.4 \text{ kg S ha}^{-1} \text{ yr}^{-1}$. The two values represent excellent agreement and give a ratio of wet : dry deposition of 1 : 1. However, if the data given by Martin (1980) and Bristow and Garwood (1984) are correct, Bromfield and Williams (1974) overestimated the S in rain by about 18 to $20 \text{ kg S ha}^{-1} \text{ yr}^{-1}$, and underestimated dry deposition by almost exactly the same amount. Perhaps the model is inapplicable to our sites because of local influences, but also of course dry deposition may have increased between 1974 and 1980. The differences emphasize the need for wet and dry deposition to be estimated separately wherever atmospheric deposition is monitored.

4.5. SOURCES OF ACIDITY

Many authors have attempted to identify sources of acidity by correlating $[\text{H}^+]$ in rainfall with various components (wet and dry) of the atmosphere (e.g., Martin, 1982, 1984; Gorham *et al.*, 1984; Pellet *et al.*, 1984). As Martin (1982) has said, "There is no way that the H^+ in rainwater can be definitely associated with a particular anion", but some idea of source can be achieved by this method. Possible sources of atmospheric pollution at the sites considered here are, at Rothamsted, agriculture and perhaps vehicle emissions (M1 motorway 3 km west, A5 trunk road 2 km west, A6 trunk road 0.5 km east), at Saxmundham, agriculture, vehicle emissions (A12 trunk road 1.5 km east) and the sea, and at Woburn, agriculture, vehicle emissions (M1 motorway 0.5 km east) and brickworks (1 km east).

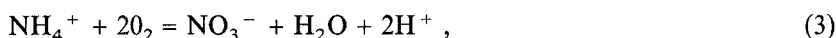
Simple correlation analyses, and more complex Principal Coordinate and Cluster Analysis, all separate the ions we measure into two main groups: Na, Mg, and Cl (sea salts) and K, Ca, NH_4 , NO_3 (earth salts); within the latter group NH_4 and NO_3 are particularly closely associated at Rothamsted and Woburn.

Precipitation acidity (H^+) correlates negatively (VAF 50%, $p < 0.05$) with sea-salts at Saxmundham and Woburn, and with earth-salts at Saxmundham; it also correlates negatively and weakly with earth-salts at Rothamsted and Woburn. Principal Coordinate and Cluster Analysis associate acidity chiefly with non-sea SO_4 , and to a much smaller extent with NO_3 and non-sea Cl. No association of acidity with anions is apparent at Saxmundham, however.

Gorham *et al.* (1984) were able to show, using cluster analysis, that the three factors determining precipitation chemistry in the Eastern U.S. were air pollution (SO_4 and NO_3), agriculture and sea-spray. Air pollution was the dominant source. We have evidence of these same three factors at our sites. At Saxmundham near the coast, sea-spray is the prime factor determining precipitation chemistry. At the two inland sites, sea-spray is still the dominant factor but agriculture is almost as important, and the association of NH_4 and NO_3 reflect the large use of NH_4NO_3 as a source of fertilizer nitrogen. The results indicate how maritime influences dominate the atmosphere over Britain, even well inland.

There is little evidence of any effect from vehicle emissions on the nearby roads. Such emissions would appear to be a truly local effect of very short range. There have been some indications that emissions of SO₂ and HF from the brickworks near Woburn inhibit crop growth there (Buckenham *et al.*, 1982) and an association of precipitation acidity with non-sea SO₄ was apparent at Woburn. However, the brickworks closed in the late 1970s but no corresponding decrease in SO₄-S in precipitation has been noticed (Figure 9). Perhaps this is another indication of the very different behavior of wet and dry deposition.

At sites such as ours, acidification of soils by direct deposition of H⁺ from the atmosphere is likely to be small (cf. Section 3.2 above). Acidity derived from nitrification of NH₄⁺ by the reaction



is potentially greater. It adds 2 eq H⁺ for every 1 eq NH₄⁺ nitrified. Acidity from deposited NH₄⁺ (5 to 15 kg ha⁻¹ yr⁻¹ at present) could therefore approach 2.0 keq ha⁻¹ yr⁻¹ at these sites, compared with directly deposited H⁺ values of 0.4 keq ha⁻¹ yr⁻¹ at Rothamsted and 0.1 keq ha⁻¹ yr⁻¹ at Saxmundham and Woburn. Johnston *et al.* (1986) have recently compared the contribution and effect on soil of the various acid inputs at Rothamsted.

Measured deposition of strong-acid anions (Cl, NO₃-N, SO₄-S) totals approximately 3.3, 4.0, and 3.0 keq ha⁻¹ yr⁻¹ at Rothamsted, Saxmundham and Woburn, respectively. Relative contributions to this, in equivalents, decrease in the order Cl⁻ ≈ SO₄²⁻ ≫ NO₃⁻. Non-sea salts comprise about 35% of the total deposition near the coast, 58% inland. Measured deposition of cations totals approximately 2.4, 3.4, and 2.3 keq ha⁻¹ yr⁻¹. The large excess of anions was discussed above (Section 4.1). At Saxmundham, where both depositions in rainfall and losses in drainage from soils in the field are measured, the amounts of Cl, NO₃-N, and SO₄-S lost in drainage water total approximately 10 keq ha⁻¹ yr⁻¹, about three times the amounts added in precipitation (Williams, 1971). This, however, balances only 55 to 60% of the cation losses (principally Ca). The excess is presumably balanced by HCO₃.

5. Conclusions

The pH of precipitation at Rothamsted is approximately 4.3 and at Saxmundham and Woburn approximately 5.0 at present. Precipitation has been becoming less acid. Precipitation acidity arises chiefly from H₂SO₄ from fuel combustion and, at Woburn in the early years of monitoring from a nearby brickworks. There is a small contribution from HCl, probably from fuel combustion, and from HNO₃, probably from vehicle exhausts. Near the East coast of England at Saxmundham, precipitation chemistry is dominated by the effects of sea-spray modified by agriculture. At the two inland sites, precipitation chemistry is again dominated by sea-spray, but with agriculture playing a much more important role than at the coast; the effects of NH₄NO₃ fertilizer are particularly noticeable.

Overall, in rural areas of predominantly arable agriculture, wet deposition of H^+ from the atmosphere is negligible. Inputs of H^+ from the nitrification of atmospheric NH_4^+ are potentially 5 to 20 times those from atmospheric H^+ , and, of course, those from the nitrification of ammonium fertilizers are far greater again.

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