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Long-term deposit at Rothamsted, southern England

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ABSTRACT

Monthly rainfall analyses are available for Rothamsted and the surrounding area since 1853. Long records exist for NH_3, NO_3 and Cl, while SO_4 and pH measurements are less complete. The most striking change over the period is a shift in the seasonal distribution of the nitrate in the rain which has changed the deposit from <0.1 g m^{-2} yr^{-1} in the mid-19th century to ~ 0.2 g m^{-2} yr^{-1} at present. The pH, initially 4.7 in 1930, starts to decline only recently by about 0.5 in the last 10–15 years. Chloride and ammonia show little change. Sulphate levels may have doubled since 1880 but there is no way to check their reliability.

1. Introduction

The increasing scale of anthropogenic activities has caused much speculation about long-term changes in the composition of the atmosphere on a synoptic or global scale. There has been considerable interest in detecting such changes through the analysis of glacial ice, sediments, tree rings, etc. It has also been possible to use past analyses of atmospheric composition to determine changes, but except for carbon dioxide and possibly ozone, historical records are considered too brief to be useful at present (Groves et al., 1978). While accurate analyses of trace gases in the atmosphere are available for less than 100 years, there are sets of precipitation analyses that are somewhat older than this. As with glacial analyses it is possible to relate precipitation composition to atmospheric composition, but with the advantage that precipitation records may be found in locations where glaciation is presently absent.

2. The data set

Observations of rainfall chemistry, particularly those pertaining to its salinity have been made in the British Isles for considerable time (e.g. Derham, 1704) and the problems in collection of samples for chemical analysis were discussed by the atomist John Dalton (1822). A complete year's contribution of chloride to the soil was determined by Madden (1843), but the first really continuous series of measurements began at Rothamsted in 1853 after the erection of a large rain gauge with an area of 0.001 acre (4.047 m^2). It is significant that not only were these analyses some of the earliest ever made, but they were continued at the same site, with gaps, to the present day.

The inspiration for this early work was the revolution in agricultural theory that followed the publication of books such as Liebig's *Die Organische Chemie in ihre Agrikultur und Physiologie*. The old ideas of plant nutrition via the humus were overthrown and new concepts put forward. Nitrogen, it was thought was taken up as ammonia from the air in much the same way as carbon dioxide, or deposited in rain. Such ideas were of great importance, as they implied that nitrogenous fertilizers were quite unnecessary. The use of fertilizers was championed by a group of workers at the fledgling experimental agricultural station at Rothamsted (Fig. 1). In addition to experiments on crop yields, they began to analyse rainfall. The earliest analyses were rather primitive, but suggested that only small amounts of ammonia were added to the soil from rain. These were an order of magnitude below that required for an optimum yield of wheat, so it was necessary to consider the contributions of nitrate to the nitrogen flux. These too were shown to be small in Way's analyses of 1855–6 (Lawes et al., 1881). There was a lull in use of the Rothamsted gauge for precipitation chemistry until it was used for measurements by Dr Frankland of the River's

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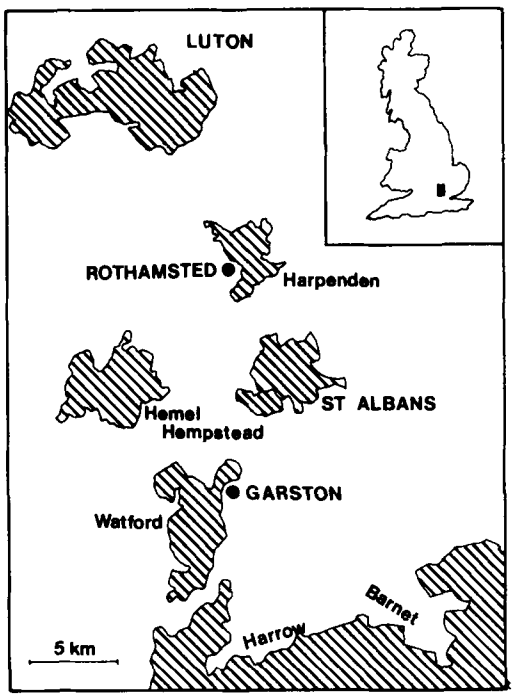

Fig. 1. Location map for rainfall collection sites (upper case) about Rothamsted. The shaded portions denote the built up areas at present.

Pollution Commission in 1869–70 and regular work on rainfall composition recommenced in 1877. The series ended in 1916 with the death of N. H. J. Miller, the principal worker at Rothamsted. It was felt that "no useful agricultural purpose could be served by continuing it in its original form" and that future interest would be concerned with changes due to pollution (Russell and Richards, 1919). Work at Rothamsted, the nearby Building Research Station (BRS) at Garston and later in St. Albans, was carried out along the lines adopted by the network set up by the Advisory Committee on Atmospheric Pollution (ACAP) which was later the responsibility of the Department of Scientific and Industrial Research (DSIR). In more recent years deposit was monitored by local government in Luton. At Rothamsted full analyses recommenced with the beginnings of the European Air Chemistry Network (EACN) and were continued in a modified form to the present.

3. Data intercomparability

It is germane to any study concerned with the assembly of a long time series that the data sets are intercomparable. Table 1 illustrates the disparate origins of the data for the Rothamsted region and emphasizes the care needed in assembling a time series. Ideally one would ask for long periods of overlap between series so that their intercomparison could be examined directly. The overlap between series B and BE spans ten years, but as both sets were analysed in the same laboratory, the correlation between these two series could not be regarded as typical. Nevertheless, it was encouraging to note a high degree of correlation; the regression coefficient for the two sets of chloride analyses being 0.90. While a number of R_5 and SA chloride measurements agreed closely they had a much lower correlation coefficient. In an earlier part of the record the overlap between undissolved solids of R_4 and G had a correlation of 0.53. The correlations were considered too weak to derive conversion factors to reduce all the data to values typical of Rothamsted. Data were used in unadjusted form which means systematic differences between the analyses still remain.

Assessment of the intercomparability of the data sets has relied on seasonal cycles because comparison of the form of different seasonal cycles would be possible even in the presence of some systematic analytical differences. The seasonal variation for a number of data sets and various chemical parameters is given in Fig. 2. The upper plot gives the seasonal variation of rainfall as a reference. The comparison between the undissolved solids (UDS) of the data sets G, SA and R_4 shows some similarity in seasonal cycle although there is a systematically higher level of undissolved solids deposited at the Building Research Station sites. The more recent data at Luton is not displayed in the seasonal graphs because the individual record lengths are rather short, but the amount of undissolved deposited matter is even higher, which is not surprising considering the urban location. The mean levels of undissolved solids in the annual deposit about Rothamsted are:

R_4 17 ± 2 g m^{-2}, G 18 ± 4 g m^{-2}, SA 20 ± 4 g m^{-2}

L_1 18 ± 4 g m^{-2}, L_2 27 ± 3 g m^{-2}, L_3 24 ± 3 g m^{-2}.

The sites have rather different levels of deposit and it is unfortunate that the earlier ones are the more rural which this gives the impression that the general level of undissolved deposit has increased, when much of the increase is due to a rural–urban shift in the gauges. Figures presented by Meetham

Table 1. *Sets of rainfall analyses used in this paper*

Location	Code	Period	Investigator	Analysis notes
Rothamsted	R_1	1853–6	T. J. Way[1]	NH_3^k, NO_3
Rothamsted	R_2	1869–70	E. Frankland[2]	NH_3^n, NO_3, UDS, Cl^a. (irregular)
Rothamsted	R_3	1876–1916	N. H. J. Miller[1]	NH_3^n, NO_3^z, Cl^a, SO_4^g (few SO_4)
Rothamsted	R_4	1919–37	ACAP/DSIR[3]	TS, Ash, DS
Rothamsted	R_5	1955–66	EACN[4]	Na, K, Ca, Mg, NH_3, NO_3, Cl, SO_4, pH etc.[e]
Rothamsted	R_6	1969–77	RES[5]	As R_5 but irregular sampling
Garston	G	1927–61	BRS[6]	TS, Ash, DS, Ca, $NH_3^{k,n}$ Cl^a, SO_4^g, pH
St. Albans	SA	1950–66	BRS[6]	TS, Ash, DS, CA, $NH_3^{k,n}$, Cl^a, SO_4^g, pH
Luton	L_{1-3}	1966–74	LG[7]	TS, Ash, DS, SO_4, pH

Abbreviations: DS, dissolved solids; TS, total solids; UDS, undissolved solids.

Data sources: (1) Miller (1905), Russell and Richards (1909); (2) Frankland (1874); (3) *Reports of the Advisory Committee on Atmospheric Pollution & D.S.I.R. Investigation of Atmospheric Pollution* (1916–1938); (4) *Tellus 8*, 112 (1965) *et seq.*; (5) Rothamsted Experimental Station, unpublished results; (6) Building Research Station, unpublished results; (7) unpublished local government results, Williams (1976).

Analytical methods: (a) argentometric titration; (e) methods adopted by the EACN, Egner and Eriksson (1955); (g) gravimetric, with barium; (k) Kjeldahl's method; (n) Nessler's method; (z) zinc–copper couple conversion to ammonia, Warrington (1889).

(1964) show the levels of deposited insoluble ash at Rothamsted halved over the years 1919–59, so despite its proximity to London, Rothamsted would appear to remain a relatively useful site for long-term study. A single value (probably low) estimated from Frankland's data suggests that the insoluble deposit at Rothamsted in the 1870s lies within the scatter of values measured there in the early part of the present century.

The seasonal variation of chlorine derived from data sets R_3, R_5 and SA which show a remarkable degree of similarity considering they are derived from two different sites and span 90 years. Not only is the seasonal pattern consistent, but the amount of deposited chlorine is of similar magnitude which suggests little change between sites. This does boost confidence in the analytical technique, but more important it suggests that the collection procedure may also be intercomparable and that is essential for comparison of all the analytical parameters. The early part of data set G has excessively high and scattered chloride and other dissolved salt levels. The reasons for this cannot be easily resolved, but were possibly in the analytical techniques. Hence only the analyses of dissolved salt after 1950 have been used, as they become intercomparable with the reliable SA data set after this time. Sulphate levels show only slight seasonal variation and are not compared in this way. Only a long-term mean sulphate value is available in R_3. The ammonia and nitrate levels of sets R_3 and R_5 are compared in Fig. 2. Despite the increased scatter, the ammonia deposit in the old and new data set seems to agree fairly well, but the nitrate shows a completely different seasonal distribution. This difference is both in the nature of the distribution of deposited nitrate and its magnitude. The distribution one may consider fairly reliable, as it should not be sensitive to changing analytical technique.

Little can be said of the comparative accuracy of the short data sets R_1, R_2, L_1, L_2 and L_3. They have been plotted in Fig. 3 but make no significant change to the overall trends. The "unreliable" early analyses of dissolved matter in G are not plotted and those in R_6 have been rejected because the concentration measurements within this data set could not be confidently converted to a mass of deposit.

4. Trends

The rainfall at Rothamsted and the large amount of available analytical data are summarized as time series in Fig. 3. The rainfall values obtained from the large gauge have smoothed with an 11-year binomial filter after missing data (1918–24, 1929)

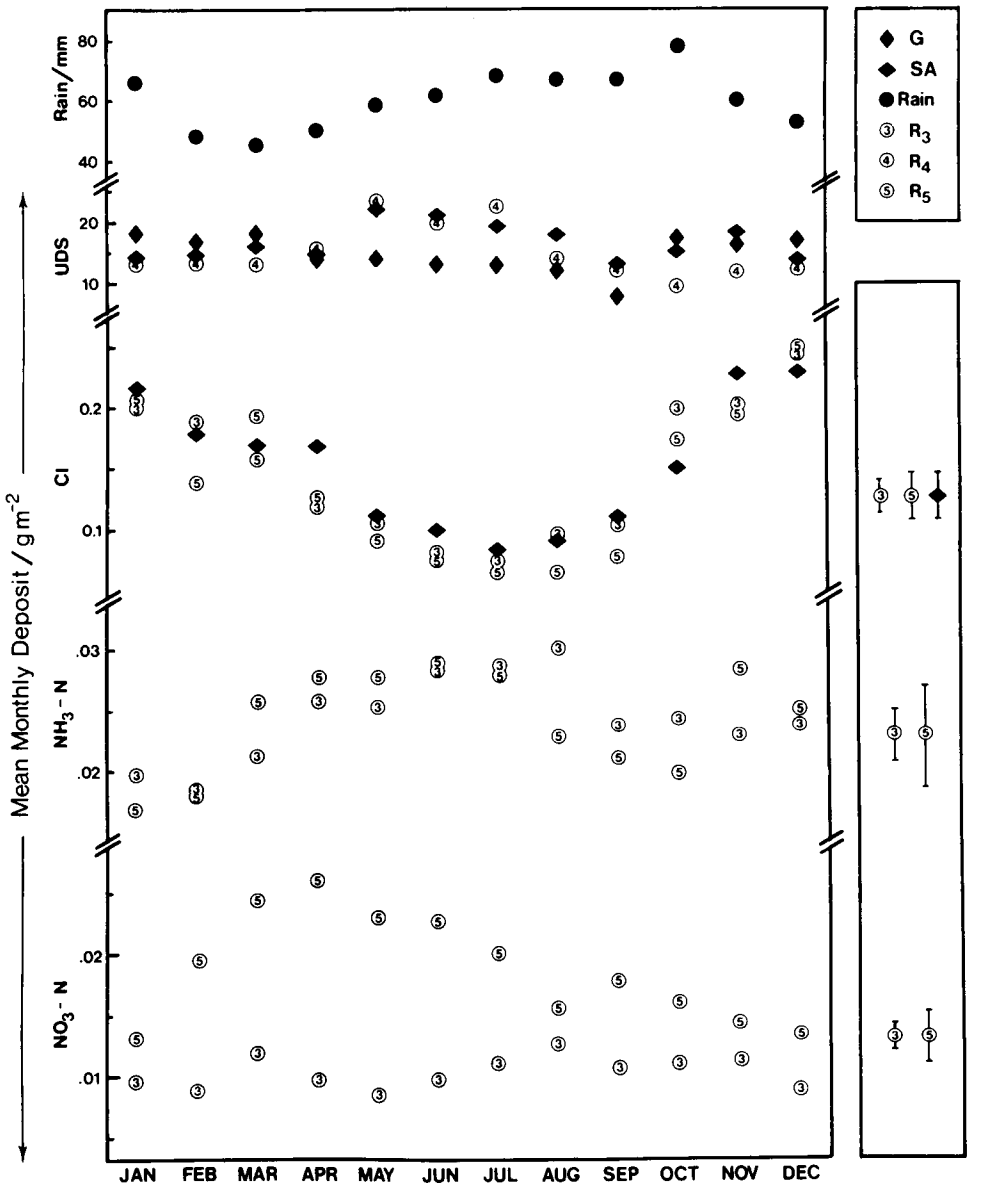

Fig. 2. Seasonal variation for a number of components of rainfall about Rothamsted. Typical standard variances of the monthly means for data points are given to the right of each annual cycle.

was interpolated by regression with the precipitation at Kew and Oxford. The rainfall changes have been relatively slight so could explain only small changes in deposit. This is particularly the case with the chloride deposit, which despite a relatively constant average shows a slight upward trend in the late 19th century (Russell and Richards, 1919). The trend does not seem to be explicable in terms of rainfall as one may regress the monthly chloride deposit with the precipitation and develop an equation to predict the annual chloride deposit (A_{Cl})

$$A_{Cl} = \sum_{m=1}^{m=12} C_m P_m + \text{const}$$

where C_m is the slope of the regression between

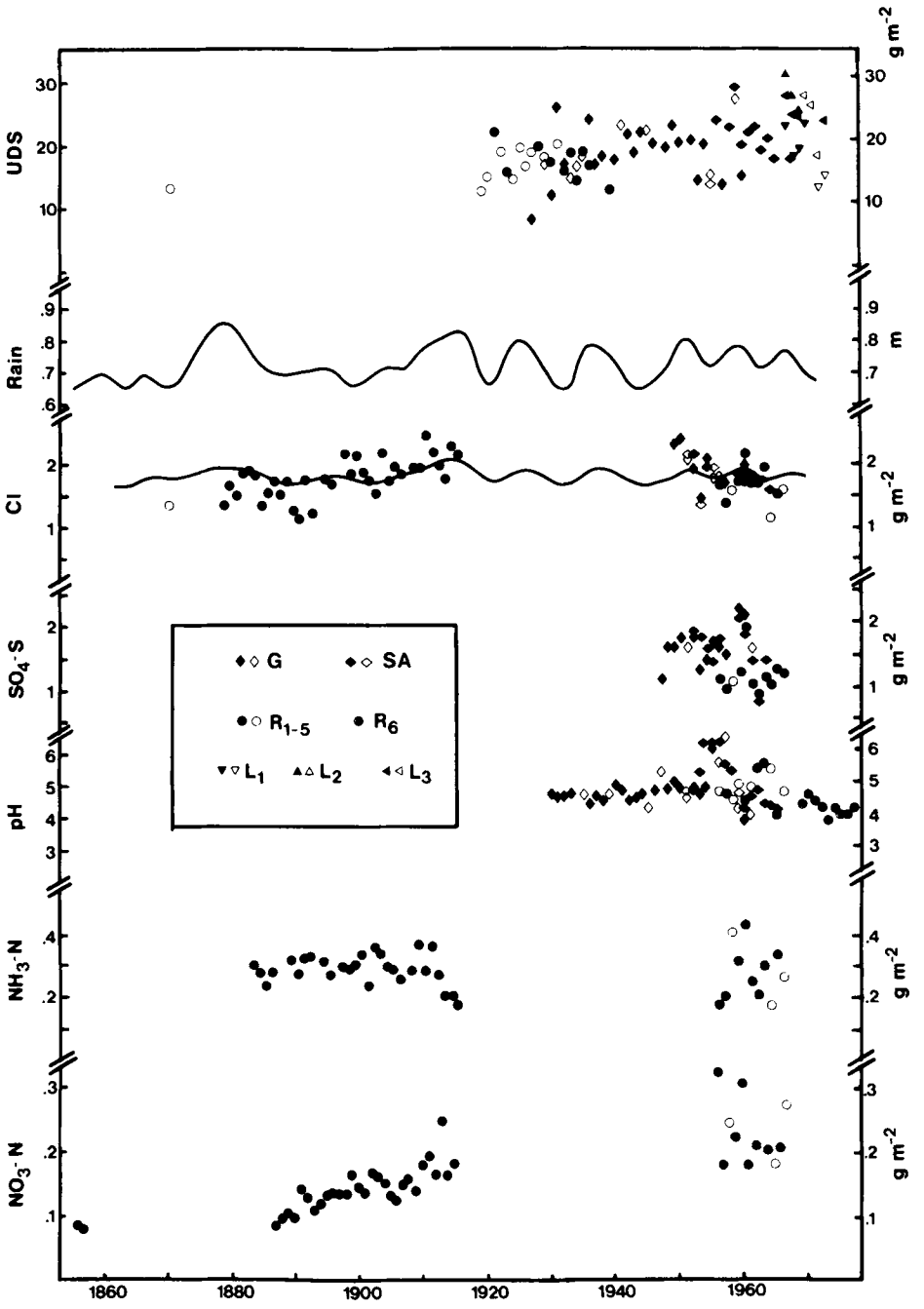

Fig. 3. Long-term variation in the annual deposit about Rothamsted. Solid symbols represent annual totals. Open symbols are those years for which only 10 or 11 months data was available and an annual total was obtained by multiplying the sum of the available measurements by $\frac{12}{10}$ or $\frac{12}{11}$ respectively, except for pH where the open symbols are the averages of the 10 or 11 available data points. The circled dots at the end of the pH time series are the R_6 measurements mentioned in the text.

chloride deposit and precipitation for month m and P_m is the precipitation amount for that month. The prediction explains about 70% of the variance in annual chloride deposit. The chloride estimated from this relationship, smoothed with an 11-year binomial filter, appears as the line through the chloride data in Fig 3. This estimate based on precipitation amounts would not appear to reproduce the gradual increase between 1877 and 1915 suggested by data set R_3.

As shown by the seasonal data, ammonia has varied little over the last century, with exception of the high values in the 1850s which Lawes et al. (1881) attributed analytical difficulties. The lack of well-defined seasonal variation in sulphur deposit and rainfall pH means that this data must be approached with further reservations. The sulphur appears much lower in the mean value (0.78 g m^{-2} yr^{-1}) determined in the 1880s at Rothamsted, than in that of the present day, but there is no way to determine the reliability of the old analyses. The present day data show little trend, which may be compared with Granat's (1978) finding that although there have been increased sulphur emissions in Europe since 1955 it has been difficult to find a corresponding trend in the deposition of sulphur in the precipitation collected at EACN sites. Although high sulphur levels may be found in R_6 (Brimblecome, 1978) there are grounds for questioning the values of soluble deposit determined from this last data set. Measurements of pH are available since 1930 and the annual average has been plotted in Fig. 3. Average pH was plotted rather than average hydrogen ion concentration as this did not weight the means towards the acidic determinations and the distribution was not normal with respect to hydrogen ion concentration. The practice of calibration of pH meters with buffer solutions should make the series reasonably intercomparable. The irregularly spaced pH measurements of R_6 were arranged so that monthly averages could be determined and from these an annual mean obtained. The pH of rainfall appears to remain relatively constant until quite recent times when there has been a decrease of about half a pH unit over about 10–15 years. This does contrast somewhat with the slight but general increase in hydrogen ion content of British rainfall noted by Martin (1979) and the recent sharp increases common in Europe, particularly Scandinavia (Barrett and Brodin, 1955). Although Martin (1979) finds that increases in the rainfall acidity on the outskirts of towns do seem to be confined to recent times, so the Rothamsted results may be characteristic of a site on an urban perimeter.

Perhaps the most interesting of the changes is the increase in nitrate deposited at Rothamsted. A similar long-term change in nitrate has been observed over the period 1957–74 at Chilton (in Oxfordshire) in the particulates collected on filter papers (Salmon et al., 1978). The change in the actual magnitude of the deposit (as illustrated in Fig. 3) may also be seen as a distinct change in the seasonal distribution in Fig. 2. It is important to note that the modern levels of nitrate deposit in the winter months approach those common late last century, while current spring values are much higher. Spring maxima in solutes in rainfall have been noted previously (Mézáros, 1974) but it seems possible to attribute the nitrate increase to an agricultural source. The application of nitrogenous fertilizers to English soils has increased thirty-fold over the last century (Russell, 1978) and now reaches 4.6 g m^{-2} yr^{-1} (Green, 1973). Almost negligible losses from soils (e.g. Bolton, 1972; Rodgers, 1978) would contribute markedly to the increase of about 0.1 g m^{-2} yr^{-1} that has occurred in the deposition of nitrates over a similar period. Greater de-nitrification activity in the spring and early summer may well explain the different seasonal distribution and the magnitude of the nitrate deposit at Rothamsted today. Another explanation for the change could lie in increased nitrate emission from fuel combustion coupled with peak photochemical activity in spring (Mézáros, 1974).

5. Conclusion

The comparison of old rainfall analyses with today's is difficult because many questions about the reliability of the older analyses seem impossible to resolve. This may restrict the conclusions that one may draw from time series assembled from such data sets, but the exercise can still be a rewarding one. The present study of deposit of Rothamsted would suggest a definite change in the seasonal distribution of nitrate in rainfall which probably corresponds to increased deposit in the spring. Chloride, as expected for an element with a largely

marine source, shows little change. Ammonia shows little change. The pH of rainfall may have decreased slightly in the most recent part of the record. The undissolved solids have decreased, but this is obscured by the less rural sites used at the end of the records. Sulphate shows an increase since 1880, but nothing is known of the intercomparability of the old and new data sets.

6. Acknowledgements

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ДОЛГОВРЕМЕННЫЕ ОСАЖДЕНИЯ В РОТАМСТЕДЕ, ЮЖНАЯ АНГЛИЯ

Для Ротамстеда и окрестностей ежемесячные анализы дождя имеются с 1853 г. Длинные ряды данных существуют для NH_3, NO_3 и Cl, в то время как данные для SO_4 и pH менее полны. Наиболее бросающееся в глаза изменение за указанный период-это сдвиг в сезонном распределении нитратов в дожде, осаждение которых изменилось с величие, меньших 0.1 $гм^{-2}$ $год^{-1}$ в середине 19 столетия, до величины порядка 0.2 $гм^{-2}$ $год^{-1}$ в настоящее время. Значение pH, равное 4.7 в 1930 г., лишь недавно начало падать и уменьшилось примерно на 0.5 за последние 10–15 лет. Хлориды и аммиак не проявляют заметных изменений. Уровень сульфатов, может быть, удвоился с 1880 г., но нет возможности проверить надежность данных.