Comparison to Longer Term Datasets

6

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Prior to the creation of the UKAWMN in 1988, few upland surface waters in the UK were regularly monitored. However a limited number of good quality datasets, some going back to the late 1970s, do exist for several areas of Scotland and Wales. Some of these sites were subsequently incorporated within the UKAWMN, while others continue to be monitored independently. Together, they provide an invaluable resource both for critically assessing the intrepretation of the UKAWMN data in the preceding chapter, and for placing the chemical changes observed in this ten year dataset into a longer term context. In the following sections, data are presented for five representative sites in central and southwestern Scotland, and in mid-Wales. Analysis of this data has been limited to visual interpretation, and should therefore be considered as a preliminary assessment.

Data for seven determinands (pH, SO_4, xSO_4, NO_3, Cl, Na and Ca) are shown for all sites (Figures 6.3, 6.4 & 6.5), whilst either DOC or a comparable measure (total organic carbon, TOC, or absorbance) are shown depending on data availability. Methods of alkalinity measurement do not appear to have been consistent between sites, and are not included.

6.1 Caorainn Achaidh Burn

The Caorainn Achaidh Burn (Loch Ard: Burn 2) has been monitored since 1979 by the Freshwater Fisheries laboratory (FFl), Pitlochry, as part of the Loch Ard group of streams (Harriman & Morrison, 1982; Harriman *et al.*, 1995a). The steep 5 km^2 catchment drains the northern slopes of Ben Lomond in central Scotland, and the sampling point is approximately 3 km west of the Loch Chon UKAWMN site. Land-use is predominantly unimproved moorland, with a small area of deciduous woodland in the lower valley. The stream was sampled once or twice per month prior to 1986, although there were two substantial unsampled periods from January 1982 to March 1983, and from May 1984 to October 1985. From 1986 to the present, samples have been collected on a weekly basis.

The most striking feature of time series for the Caorainn Achaidh Burn (Figure 6.1) is a marked decline in sulphate concentrations, which is consistent with the declining trend reported by Harriman *et al.* (1995a). Between 1979-1982, mean xSO_4 was 115 $\mu eq\ l^{-1}$, but by 1996-1998 this had more than halved, to 53 $\mu eq\ l^{-1}$. Virtually all the decline took place prior to 1989, since when concentrations have remained relatively constant. These patterns of variation are consistent with the near-constant xSO_4 levels observed from 1988-1998 at the nearby Lochs Chon and Tinker, but suggest that large xSO_4 reductions may well have occurred at the two UKAWMN lochs before sampling began. Despite the change in xSO_4 at the Caorainn Achaidh Burn there is little evidence of an increase in pH, possibly due to large, short term episodic variation at this steep, flashy catchment. NO_3 appears to have experienced large inter-annual variations in peak concentrations, perhaps linked to climatic factors (Section 5.4), but there is no indication of an overall rising trend.

Variations in Cl and Na closely match those at Lochs Chon and Tinker, with peaks in 1989 and 1993, but in general peak concentrations are very much higher, and background concentrations somewhat lower. This variability may again reflect the steep, thin soils of the catchment which (together with the absence of a lake) provide limited storage of water between rain events. Although there appears to be some year-to-year variability in marine ion concentrations, the impact of sea-salt inputs may largely be restricted to episodic timescales, rather than the significant inter-annual cycles observed at the less hydrologically responsive UKAWMN catchments.

Finally, although monitoring of DOC only began during late 1985, there has since been a very

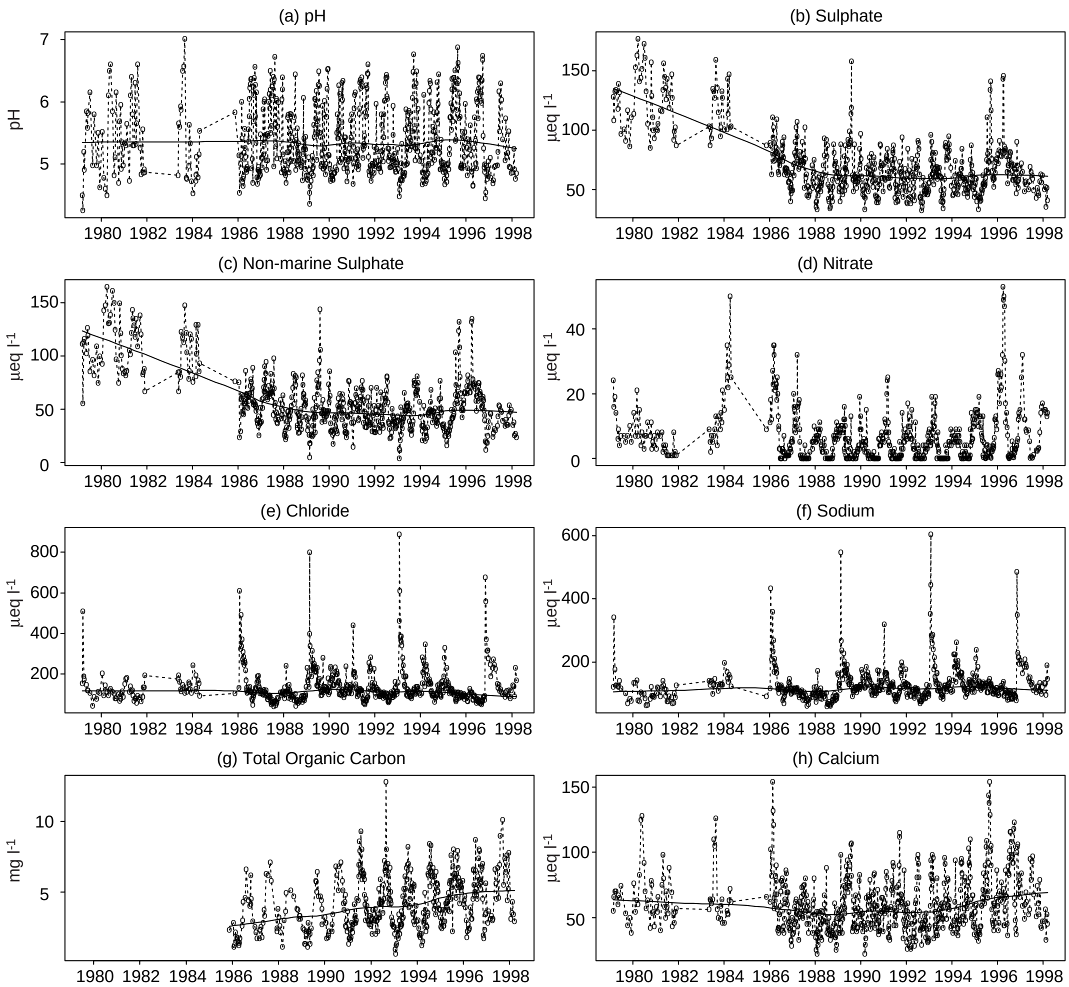


Figure 6.1

Long term trends, Caorainn Achaidh Burn

Smoothed line represents LOESS curve (Section 3.1.2)

marked and approximately linear increase at this site. This is highly consistent with observations at the Trossachs lochs and elswhere in the UKAWMN, suggesting that organic carbon concentrations began rising some time prior to the creation of the UKAWMN, and that changes do not simply reflect a short term fluctuation.

6.2 Round Loch of Glenhead

Round Loch of Glenhead, Galloway, is a peaty moorland site forming part of the UKAWMN (Section 4.7), and has been monitored by FFl since 1979. Prior to 1988 sampling was intermittent, with three samples collected in 1979 and one to three per year from 1984 to 1987. From 1988 onwards, sampling has been maintained at approximately a monthly frequency. (UKAWMN sampling during this time took place quarterly).

Long term data for Round Loch (Figure 6.2) show a major decline in SO_4 concentrations. As at the Caorainn Achaidh Burn, virtually all the decrease appears to have taken place before UKAWMN monitoring began in 1988. However, at Round Loch, this change appears to have been accompanied by a rise in pH levels, indicating overall chemical recovery and this is consistent with palaeoecological evidence from diatom pH reconstruction that some recovery had taken place at the site by the late 1980s (Battarbee *et al.*, 1988). A very clear cycle in Cl and Na, peaking in 1990-1991, matches that observed in the UKAWMN data, and there appears also to have been an earlier peak in 1984. Ca concentrations are moderately correlated with Na

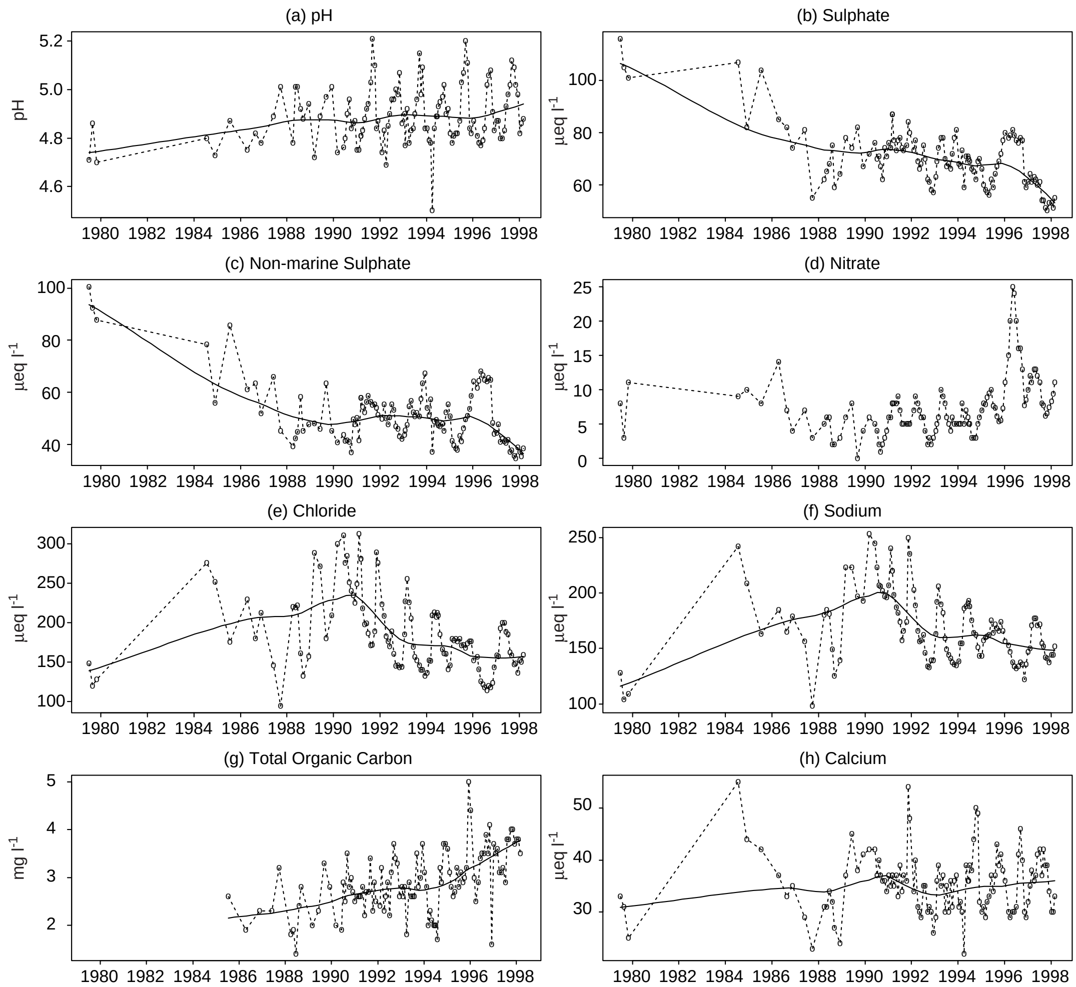


Figure 6.2

Long term trends, Round Loch of Glenhead

Smoothed line represents LOESS curve (Section 3.1.2)

and Cl, and some inverse correlation between xSO_4 and Cl is evident from 1988 onwards.

Monthly data for Round Loch confirm that NO_3 has risen substantially since 1988. However, relatively high concentrations earlier in the record argue that this rise may not be driven by catchment nitrogen saturation, and instead may be linked to climatic fluctuations. The increase in DOC observed in the UKAWMN data is shown to have occurred more or less linearly since sampling began in 1984.

■ 6.3 Dargall Lane

Dargall Lane, a moorland catchment containing a mixture of podzols, peaty gleys and blanket peats, has been monitored since the early 1980s as part of the Loch Dee Project, coordinated by the Solway River Purifaction Board (Lees *et al*., 1989). For this study, stream chemistry data for 1983 to 1998 have been obtained from the Scottish Environmental Protection Agency (SEPA), South West Region. Samples have been collected at weekly intervals throughout this time, and since this monitoring has taken place separately from UKAWMN monitoring at the same site (Section 4.9), this dataset provides an excellent validation, as well as an extention, of the UKAWMN data. An analysis of trends at Dargall Lane and adjacent sites was undertaken by Langan *et al*. (1997), and indicated a reduction in xSO_4, no trend in pH or NO_3, and strong inter-annual cyclicity in sea-salt ions.

Time series (Figure 6.3) support these findings, indicating that SO_4 and xSO_4 have declined at Dargall Lane, although to a somewhat lesser

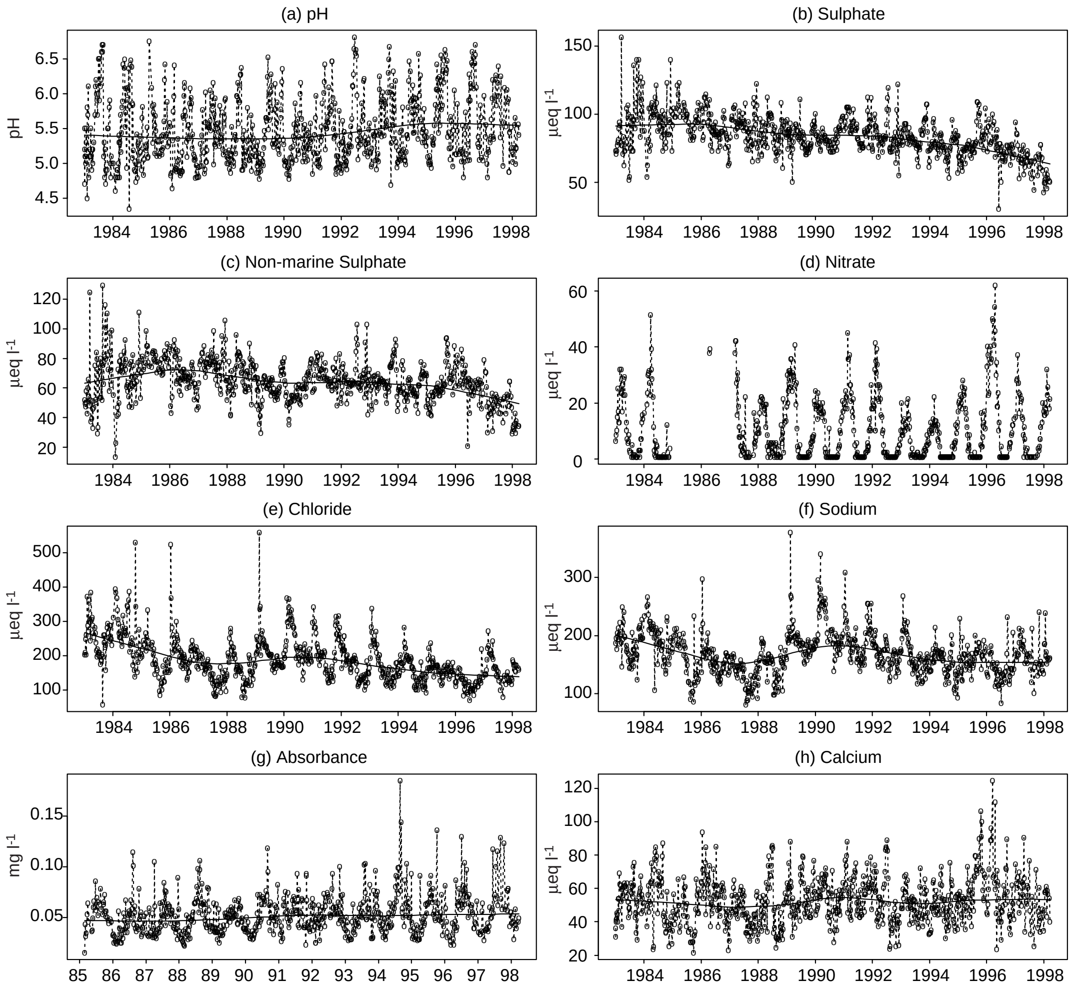


Figure 6.3

Long term trends, Dargall Lane

Smoothed line represents LOESS curve (Section 3.1.2)

degree than at the preceding sites. There is weak evidence for an increase in stream pH, which may to some extent have been masked by large episode-scale variations. Cyclicity in Cl and Na is clearly evident, indicating that climatically driven fluctuations in sea-salt inputs have a major influence on stream chemistry. The 1990 peak in these ions is consistent with that observed in the UKAWMN data, with an additional peak apparent in 1983-1984. Both Cl peaks correspond to periods of low xSO_4, and in general there is a good inverse correlation between these anions. No overall trends are observed for either NO_3 or Ca, although the latter appears weakly correlated with Na and Cl. An apparent increase in absorbance over the monitoring period is consistent with observations of rising DOC in the UKAWMN data.

6.4 Afon Hafren

The Afon Hafren, in mid-Wales, is a predominantly forested catchment containing a mixture of peaty podzols and peats, and has been monitored as part of the UKAWMN since 1988 (Section 4.17). Additional sampling of this stream has been carried out by the Institute of Hydrology on a weekly basis since 1983. A Seasonal Kendall analysis of data for 1983-1993 was undertaken by Robson & Neal (1996), who identified an increasing trend in DOC, and inversely related fluctuations in Cl and xSO_4. The 1983-1998 data presented here (Figure 6.4) are consistent with these observations, indicating that DOC has continued to rise throughout the 15 years. Very pronounced cyclicity is observed for Cl, Na and xSO_4, with Cl peaks in 1984 and 1990

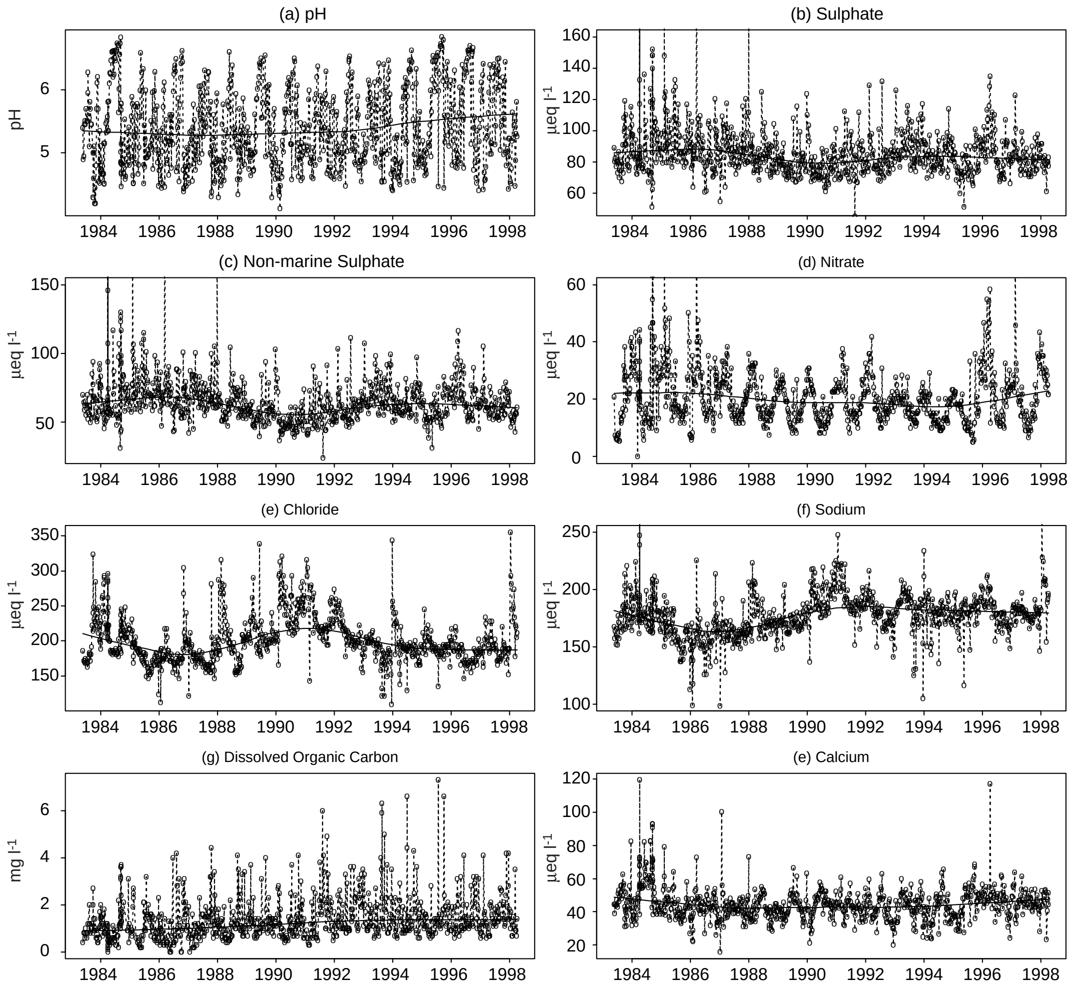


Figure 6.4

Long term trends, Afon Hafren

Smoothed line represents LOESS curve (Section 3.1.2)

corresponding to xSO_4 minima, and also to the Cl peaks observed at Dargall Lane. There is little evidence of an overall decline in xSO_4 at the Hafren, and together with high levels of episodic variation this may account for the lack of detectable recovery in pH. There are also no clear trends in either NO_3 or Ca.

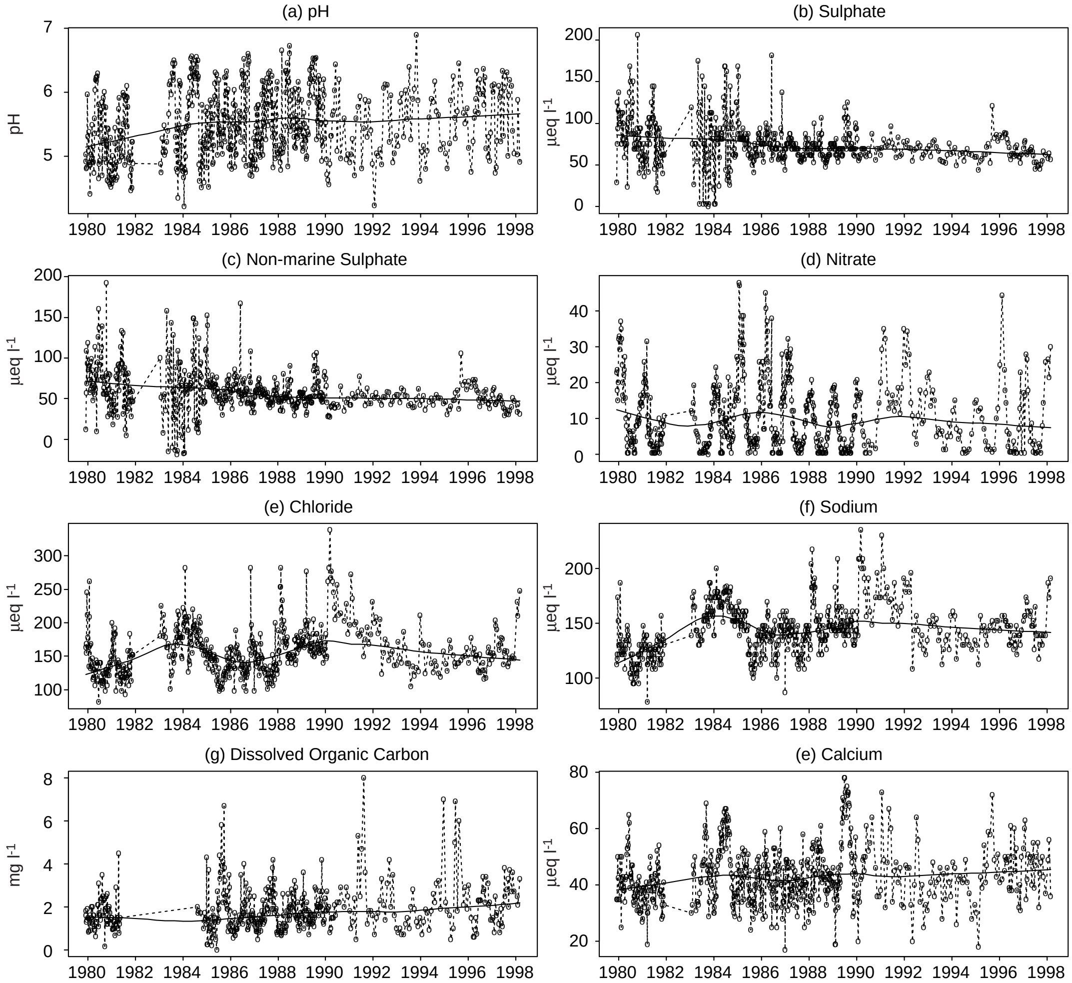
6.5 Afon Gwy

The Afon Gwy, a moorland catchment with peaty podsol and peat soils adjacent to the Hafren, has been monitored by the Institute of Terrestrial Ecology since late 1979. Apart from missing data during 1982, the stream was sampled weekly until 1990, and monthly thereafter. The site became part of the UKAWMN in April 1991 (Section 4.18). A Seasonal Kendall trend analysis was undertaken for the 1980-1996 dataset by Reynolds *et al.*, (1997), who identified a significant decrease in xSO_4, and increases in pH and DOC.

The 1979-1998 data presented here (Figure 6.5) expand only slightly on those analysed by Reynolds *et al.* (1997), and their findings remain applicable. Although sulphate data appear rather noisy in the early part of the record there has clearly been a decrease over the monitoring period, and this has been accompanied by a substantial rise in pH. However, as at other sites, most of the change seems to have occurred during the early to mid 1980s. Pronounced cyclicity in Na and Cl is observed throughout the record, and as at other sites the main peaks appear to have occurred in 1984 and 1990-1991. Large variations in annual peak NO_3 concentrations have also been observed, but there

Figure 6.5

Long term trends, Afon Gwy



is no overall trend. DOC concentrations appear to have risen, although as indicated by the UKAWMN trend analysis the magnitude of this change has been relatively small.

6.6 Summary

Based on the five sites considered here, the following general conclusions can be drawn with regard to the interpretation of UKAWMN data in the preceding chapter.

- Where higher frequency datasets exist for UKAWMN sites (Dargall Lane, Round Loch of Glenhead, Afon Hafren and Afon Gwy), these correspond well with UKAWMN data. This suggests that the current UKAWMN sampling frequencies (monthly at rivers, quarterly at lakes) adequately capture overall patterns of long term variation, although an increased frequency would allow a more sensitive detection of trends.

- It appears that the relatively stable xSO_4 concentrations observed during the 1988-1998 period of UKAWMN operation are not necessarily representative of longer term trends. Most of the sites considered here exhibited large xSO_4 reductions during the early to mid-1980s, corresponding to large deposition reductions at this time (RGAR, 1997). At a number of sites, an associated pH increase has been observed. Since the mid-1980s, there has been little further decline in sulphur deposition at these sites (Chapter 2), all of which are in west coast locations, remote from major emission sources. However future reductions in sulphur deposition on a similar scale to those observed in the early 1980s can be expected to lead to further decreases in surface water xSO_4, and subsequently to increases in pH.

- Climatically driven cyclicity in marine ions is observed in varying degrees at all five sites. The large 1990 peak observed at many UKAWMN sites occurs in all longer term datasets, in addition to which a peak of similar magnitude can be identified for 1983-1984. Like the 1990 peak, this corresponds to a peak in the winter North Atlantic Oscillation and can be attributed to an increased frequency of westerly storms at this time. The presence of this earlier peak implies that levels of climatic and chemical variability observed in the 1988-1998 data are probably typical over the longer term. Additional peaks in marine ions observed at the Caorrainn Achaidh Burn are consistent with those observed at the two Trossachs UKAWMN sites.

- In general, the inverse relationship between marine ion and xSO_4 concentrations suggested by the UKAWMN data is strongly supported. This climatically driven fluctuation in calculated xSO_4 is believed to be driven by short term adsorption and desorption of marine SO_4, which leads to an overestimate and underestimate of the marine SO_4 component respectively (Section 5.3.4) and is effectively superimposed on longer term, deposition driven trends.

- No trends are observed in NO_3, indicating that catchment soils and vegetation continue to immobilise a high proportion of N inputs. It is uncertain whether continued N deposition will ultimately cause increased NO_3 leaching, which might counteract any improvement in runoff acidity resulting from xSO_4 decreases. Large inter-annual variability in NO_3, linked to climatic factors, demonstrate the need for continued high quality long term monitoring if evidence of nitrogen saturation is to be detected against a background of natural fluctuations.

- All five sites exhibit increases in DOC or a comparable determinand, supporting the intrepretation that long term, monotonic increases are occurring at many UKAWMN sites.