Water Chemistry Discussion

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■ 5.1 Regional Variability in Surface Water Chemistry

5.1.1 Acidity and Non-marine Sulphate

The UKAWMN, with only 22 sites in acid sensitive parts of the UK, was not designed to permit a statistically robust assessment of spatial variations in surface water chemistry across the UK. However, some general spatial patterns are observed, and maps showing mean values for a number of important variables are presented in Figure 5.1. Mean values for a wider range of determinands are given in Table 5.1.

Inter-site variability in mean alkalinity is actually quite low; with the exception of Coneyglen Burn (alkalinity 161 μeq l^{-1}), all site means fall within the range -30 to 48 μeq l^{-1}. However, this alkalinity band is associated with a wide range in pH, from 4.6 to 6.5, which in turn represents a variation in H$^+$ concentration of approximately two orders of magnitude (0.3 to 25 μeq l^{-1}). Similar variability is observed for labile Al (3 to 287 μg l^{-1}).

Mean Acid Neutralising Capacity (ANC) has been calculated as the sum of base cations minus the sum of acid anions. Although alkalinity, as a directly measured variable, was used in preference to ANC for trend analyses, ANC is widely used as an indicator of surface water acidity status and to relate water chemistry to biological status. Table 5.1 demonstrates a close relationship between alkalinity and ANC, with spatial variations in ANC largely replicating those for alkalinity. With the exception of Coneyglen Burn (204 μeq l^{-1}), ANC varies from –52 to 63 μeq l^{-1} between sites. This range is somewhat greater than for alkalinity.

Concentrations of xSO$_4$ (Figure 5.1a) generally increase across the mainland UK from northwest to southeast, with a similar gradient suggested from the sites within Northern Ireland. These patterns are consistent with measured emission and deposition variations across the UK (Chapter 2), although other factors such as forestry deposition enhancement, internal sulphur sources and evaporation (notably at Old Lodge) can also increase surface water concentrations to varying degrees. To a first approximation, sites with higher xSO$_4$ concentrations tend to be more acidic, in accordance with the role of xSO$_4$ as the main acidifying anion. However, this link is complicated by variations in catchment buffering capacity, represented in Table 5.1 by xCa. For example, Burnmoor Tarn has higher xSO$_4$ concentrations than nearby Scoat Tarn but, due primarily to higher xCa levels, is much less acidic. The importance of catchment buffering is reflected in the complex spatial variability observed for mean pH (Figure 5.1b).

5.1.2 Nitrate

Spatial variations in NO$_3$ (Figure 5.1c) show a reasonable correlation with N deposition; consistently low concentrations are observed in the relatively low deposition regions of northwest Scotland and northwest Northern Ireland, while maximum concentrations occur at the highly deposition impacted River Etherow. However, between these extremes there is significant inter-site variability which can be attributed to catchment specific conditions. Factors likely to enhance NO$_3$ concentrations at a given site include deposition enhancement at forested catchments (Section 5.5) and lower levels of biological uptake of N at high altitude sites such as Scoat Tarn and Lochnagar (Kernan & Allott, 1999). The mean proportional contribution of NO$_3$ to total anthropogenic acidity (i.e. NO$_3$ as a percentage of [NO$_3$ + xSO$_4$]) also varies widely, from 4% to 34% (Figure 5.1d). No clear spatial pattern is evident, with NO$_3$ contributing most significantly to acidity at Scoat Tarn, Blue Lough, the Bencrom River and the Afon Hafren, and least at the Allt a'Mharcaidh and Old Lodge. NO$_3$ is not the dominant cause of

Figure 5.1
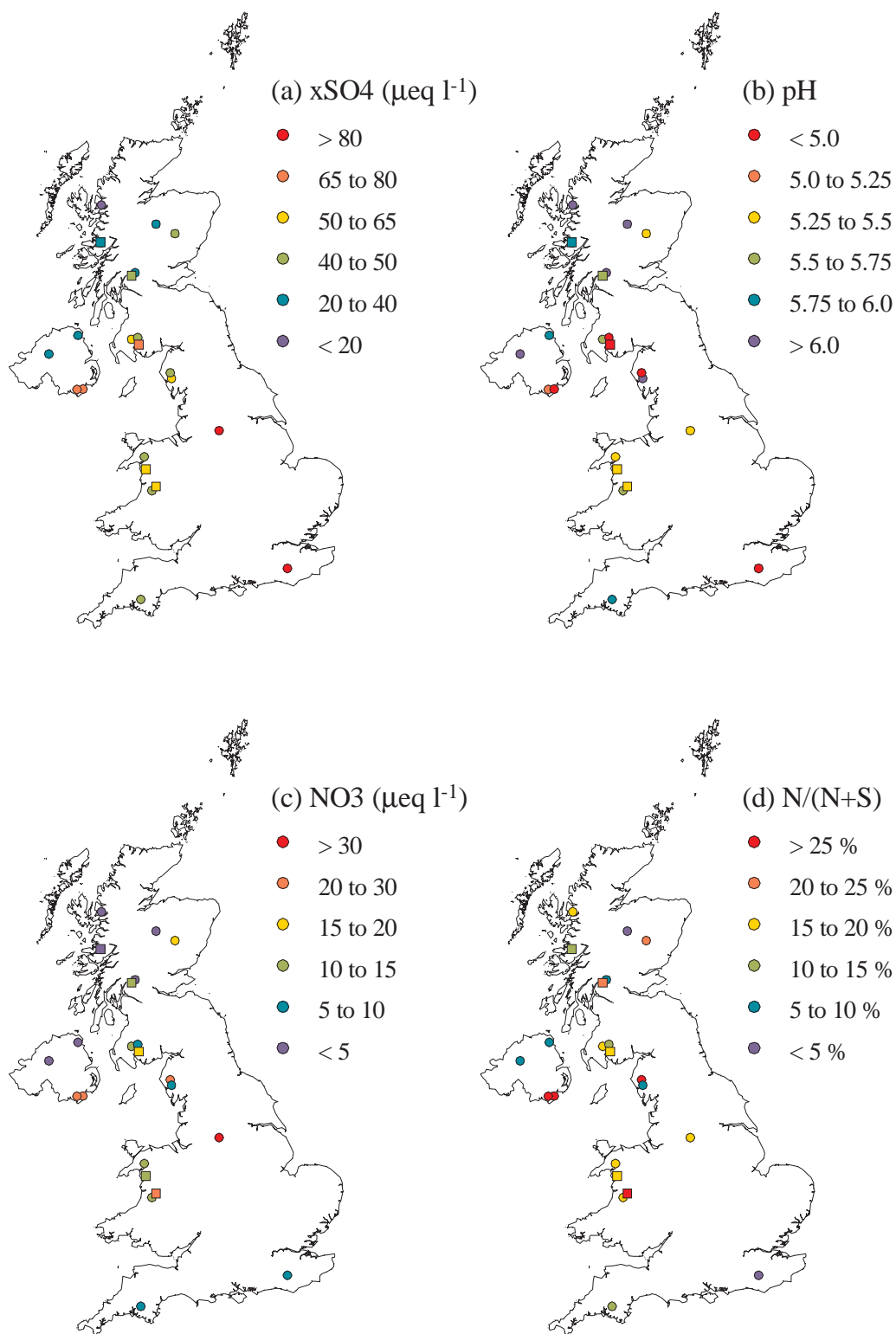**1988-1998 mean values for xSO$_4$, pH, NO$_3$ and N/(N+S) for UKAWMN sites**

(a) xSO4 (μeq l^{-1})

- > 80
- 65 to 80
- 50 to 65
- 40 to 50
- 20 to 40
- < 20

(b) pH

- < 5.0
- 5.0 to 5.25
- 5.25 to 5.5
- 5.5 to 5.75
- 5.75 to 6.0
- > 6.0

(c) NO3 (μeq l^{-1})

- > 30
- 20 to 30
- 15 to 20
- 10 to 15
- 5 to 10
- < 5

(d) N/(N+S)

- > 25 %
- 20 to 25 %
- 15 to 20 %
- 10 to 15 %
- 5 to 10 %
- < 5 %

Table 5.1

Mean chemistry (1988 - 1998) of UKAWMN sites

All variables in μeq l⁻¹ except labile Al (μg l⁻¹) and N% (NO₃ as a percentage of [NO₃ + xSO₄], measured in μeq l⁻¹).

SITE	Alkalinity	ANC	pH	labile Al	xSO_4	NO_3	N%	Cl	xCa
Loch Coire nan Arr	38	43	6.4	3	14	3	17%	258	32
Allt a'Mharcaidh	44	58	6.5	7	33	1	4%	110	38
Allt na Coire nan Con	22	34	5.9	17	30	4	12%	296	46
Lochnagar	1	1	5.3	26	48	16	25%	89	25
Loch Chon	10	20	5.6	20	49	12	20%	223	69
Loch Tinker	38	63	6.1	3	39	3	7%	163	78
Round Loch of Glenhead	-12	-9	4.9	60	47	7	13%	195	25
Loch Grannoch	-28	-14	4.6	225	72	17	19%	257	38
Dargall Lane	4	4	5.5	33	60	11	15%	186	42
Scoat Tarn	-8	-15	5.0	109	41	21	34%	186	25
Burnmoor Tarn	48	59	6.5	3	59	5	8%	210	81
River Etherow	7	29	5.5	66	240	49	17%	310	160
Old Lodge	-30	-52	4.6	195	193	7	4%	571	129
Narrator Brook	16	19	5.8	27	45	6	13%	274	24
Llyn Llagi	6	9	5.3	40	41	10	20%	194	45
Llyn Cwm Mynach	5	7	5.4	65	54	10	16%	304	58
Afon Hafren	6	-3	5.4	99	60	21	26%	209	37
Afon Gwy	12	11	5.6	56	48	11	18%	159	33
Beagh's Burn	44	114	5.8	10	38	4	9%	337	89
Bencrom River	-5	11	5.2	125	67	29	30%	255	42
Blue Lough	-23	-29	4.7	287	66	29	30%	276	29
Coneyglen Burn	161	204	6.5	8	30	3	9%	255	139

acidity at any site, although concentrations temporarily exceed those of xSO₄ during spring episodes at Scoat Tarn and the Bencrom River.

Whereas S inputs and outputs in most UK upland catchments are believed to be in long term balance (Jenkins *et al.*, 1997a), a significant proportion of incoming N deposition is retained or removed by the catchment biota through processes including vegetation uptake, microbial immobilisation and denitrification (Jenkins *et al.*, 1997b; Stoddard, 1994). In pristine environments nitrogen may be a limiting nutrient (Tamm, 1992), in which case virtually all N inputs are retained. However, it has been suggested (Skeffington & Wilson 1988; Aber *et al.*, 1989)

that elevated atmospheric inputs from anthropogenic sources can lead to conditions of 'nitrogen saturation', allowing increasing release of NO₃ to surface waters with resultant acidification. Stoddard (1994) identified four stages of nitrogen saturation in upland systems. According to this scheme, Stage 0 is the unimpacted condition, in which strong ecosystem retention causes runoff concentrations to remain at or close to detection limits. At Stage 1, N supply exceeds demand during winter but catchments remain N-limited during summer, so that runoff concentrations vary seasonally, from near-zero during summer to maxima in late winter/early spring. Stage 2 saturation occurs when catchments cease to be N-limited at any

time, causing summer minima to rise above detection limits, whilst at Stage 3, catchments are fully saturated throughout the year, with continuously high runoff concentrations and limited seasonality.

The quarterly sampling regime at UKAWMN lake sites may be considered insufficient for identification of saturation stages. Furthermore, seasonal N dynamics can be significantly altered by storage within larger lakes, for example by maintaining NO_3 above detection limits during summer (Momen *et al.*, 1999), even though the terrestrial system may be N-limited at this time. Data for the monthly sampled UKAWMN streams are therefore considered to be more suitable for an assessment of catchment saturation status, and time series (Figure 5.2) appear to conform well to Stoddard's classification. According to the definitions given, the Allt a'Mharcaidh is clearly at Stage 0. Coneyglen Burn also appears to be at Stage 0 prior to a large episodic nitrate pulse in 1996 (Section 4.22). It is unclear as yet whether this event represents the onset of a permanent change in nitrogen status at this site, or simply a short term perturbation. Generally low concentrations but small winter peaks at Beagh's Burn, Allt na Coire nan Con and Narrator Brook suggest that these sites are transitional between Stages 0 and 1, whilst Old Lodge, the Afon Gwy and Dargall Lane all exhibit the strong seasonality and near-zero summer concentrations characteristic of Stage 1. The Afon Hafren and Bencrom River, with concentrations above detection limits at all times, appear to be at Stage 2, whilst the continuously high concentrations and lack of seasonality at the Etherow indicate that this site is at Stage 3.

It appears then, that the full range of N leaching conditions are represented within the 11 streams of the UKAWMN, from full retention at low deposition locations to severe leaching in high deposition areas. The general correlation observed between N inputs and outputs at UKAWMN sites suggests that a space-for-time substitution similar to that used by Stoddard (1994) may be reasonable. This would suggest that sites currently at lower stages of N saturation would be likely, under increased or even continued current levels of N deposition, to move to more advanced saturation stages in the future.

■ 5.2 Temporal Trends in Surface Water Chemistry

5.2.1 Acidity and Non-marine Sulphate

(i) Observed Changes, 1988-1998.

Trend analyses demonstrate increases in pH and alkalinity at six and four sites respectively, while four sites show trends in both. On initial assessment this provides encouraging evidence of chemical recovery. However, only three sites exhibit declines in xSO_4, while none show declines in NO_3, and no sites exhibit both reductions in acidity and declining trends in acid anion concentrations (Table 5.2). This is perhaps surprising given that decreases in UK sulphur emissions since the 1970s (RGAR, 1997) should in theory have led to reductions in surface water xSO_4 levels, and subsequently to reduced acidity. In the absence of decreasing xSO_4 trends, the observed pH and alkalinity increases cannot confidently be attributed to deposition reductions, and at some sites may instead be the result of variations in sea-salt inputs and/or rainfall (Section 5.3). The lack of clear widespread decreases in xSO_4 appears to be linked to several factors:

- *Reductions in sulphur deposition at many UKAWMN sites between 1988 and 1998 may have been relatively small*. As noted in Chapter 2, UK sulphur emissions have decreased by 55% between 1986-1997, and total deposition by around 50%. However, more of this reduction has been in dry deposition, which for the UK as a whole has declined by 61%, while wet deposition has only declined by 42%. In 1986 wet and dry deposition inputs were approximately equal, but in the remote, high-rainfall upland areas where most UKAWMN sites are located, wet deposition provides a greater proportion of the total input. Consequently, total deposition reductions in these regions have been much smaller than the national average, and at many sites no trend at all can be detected in wet deposition over the
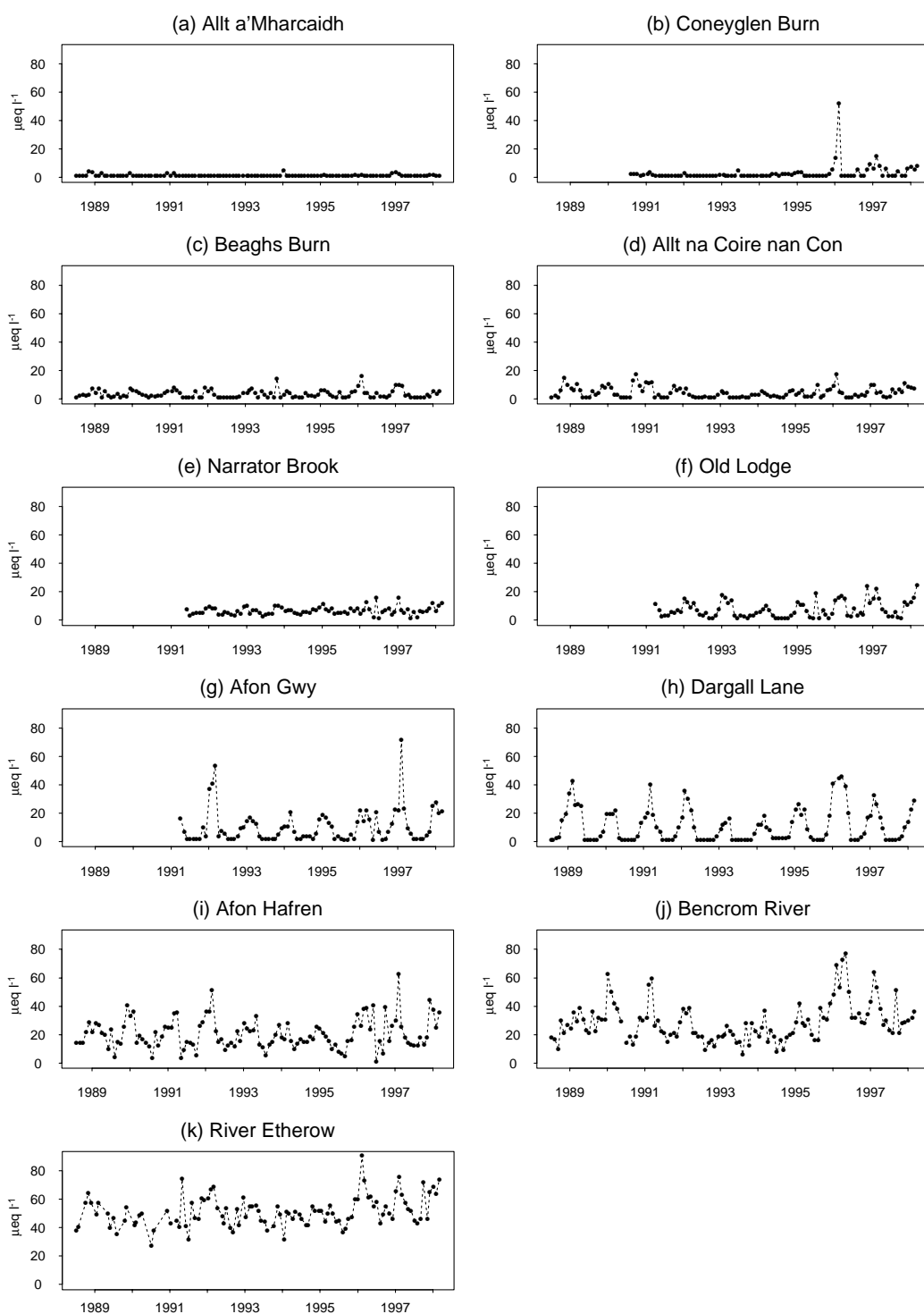
Figure 5.2

NO$_3$ time series (1988-1998) for UKAWMN streams

Table 5.2

Sites with increasing alkalinity, increasing pH or decreasing xSO$_4$, for the period 1988-1998, according to trend analysis (SKT = Seasonal Kendal Test; REG = Linear regression)

Site	Alkalinity (µeq l^{-1})		pH		xSO$_4$ (µeq l^{-1})	
	SKT	REG	SKT	REG	SKT	REG
Loch Chon	+1.0*	+1.4*	+0.044*	+0.04*		
Blue Lough		+1.2*		+0.02*		
Narrator Brook		+1.8*		+0.06**		+1.0**
Dargall Lane	+0.9*					
Scoat Tarn			+0.013*	+0.02*		
Llyn Llagi			+0.049*			
Afon Gwy				+0.05*		
River Etherow					-5.9**	-7.9**
Lochnagar				-0.02*	-0.5*	-1.0*
Old Lodge						-8.8*

*Trend significant at p < 0.05; ** trend significant at p < 0.01; *** trend significant at p < 0.001.*

last decade (Chapter 2). Lochnagar, the River Etherow and Old Lodge, which have central or eastern locations, receive proportionally higher dry deposition inputs, and have experienced greater total deposition reductions, and detectable reductions in surface water xSO$_4$ concentrations.

• *Short term variations are large relative to long term changes*. This problem is particularly severe at sites with relatively low xSO$_4$ concentrations. 13 of the UKAWMN sites have mean xSO$_4$ concentrations below 50 µeq l^{-1}. Even proportionally sizeable reductions at these sites are unlikely to be much larger than their mean standard deviation (of 13.1 µeq l^{-1}) over the decade. This demonstrates how even quite large trends may be difficult to detect By contrast, the observed decline in xSO$_4$ at the Etherow represents an absolute decrease of around 60 µeq l^{-1}, which is more readily identifiable.

• *The marine-ion correction, used to calculate xSO$_4$, is influenced by decadal-scale climatic variations at coastal sites*. There is evidence to suggest that soil retention and release of SO$_4$, driven by varying levels of sea-salt deposition, causes cyclicity in calculated xSO$_4$ concentrations which may mask anthropogenically driven changes. Unusually high levels of marine ion deposition during the first three years of monitoring appear to have suppressed xSO$_4$ estimates at this time, causing particular problems for trend detection. This subject is discussed further in Section 5.3.3.

• *Soils may be releasing stored sulphur*. Although UK soils are widely assumed to be saturated with respect to adsorbed SO$_4$, a reduction in deposition inputs may result in over-saturation, and therefore some S desorption. This may damp the effect of deposition reductions at some sites.

Even at the three sites with decreasing xSO$_4$ (Lochnagar, the River Etherow and Old Lodge), recovery in pH or alkalinity has not yet been observed. In Scandinavia and the United States, surface water chemistry recovery following xSO$_4$ reductions has been delayed by accompanying decreases in base cations (Stoddard *et al.*, 1999). This can be attributed to reduced total cation export as mobile anion concentrations decline; as soil base saturation levels are re-stocked from primary weathering, surface water base cation
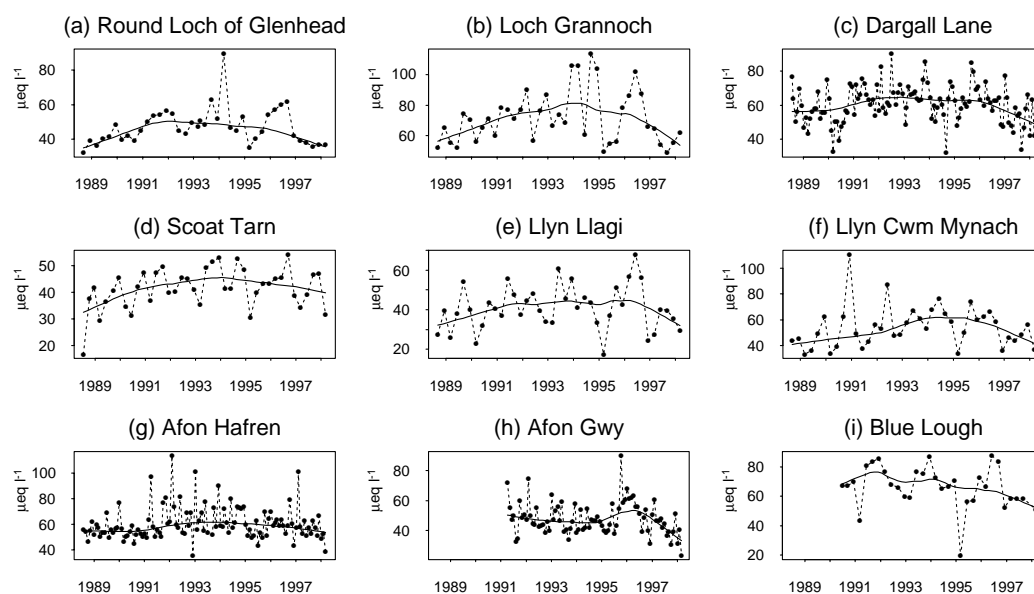
concentrations can be expected to stabilise, permitting further recovery in pH and alkalinity (Galloway *et al.*, 1983). Downward trends in Ca and Mg at the Etherow and Old Lodge (Tables 5.12.3, 5.13.3) suggest similar patterns here, although these trends are relatively weak, and detected only using regression analysis. At all three sites, however, there are strong indications that NO_3 concentrations have increased over the monitoring period. This appears to have offset the effects of decreasing xSO_4, and indeed at Lochnagar the rise in NO_3 has exceeded the fall in xSO_4, causing further acidification.

(ii) Prospects for future recovery

Although there has been little indication of recovery at the UKAWMN sites during the last decade, this should become evident with continued monitoring. As noted above, the apparent increase in xSO_4 at many sites during the early part of the monitoring period may have been the result of a very high sea-salt deposition period 1989-1991, during which marine SO_4 was initially retained by catchment soils, relative to marine Cl (reducing the estimate of xSO_4), and subsequently released (enhancing the estimate of xSO_4). In this context, the xSO_4 reductions at many UKAWMN sites since the mid-1990s (Figure 5.3) are encouraging, and may well

represent the resumption of a long term declining trend. Longer term datasets, described in Chapter 6, provide further evidence that the period of rising xSO_4 during the early 1990s represents the temporary disruption of a long term downward trend, and that this downward trend has had, and will continue to have, a positive impact on surface water acidity. Large forecast emissions reductions under the UNECE multipollutant, multi-effect protocol suggest that these recovery trends should continue in future years, becoming statistically significant at an increasing number of sites.

(iii) Variations in ANC

Although trend analysis of ANC was not undertaken, time series (Figure 5.4) show similar variations to those observed for alkalinity. The majority of sites exhibit a degree of cyclicity in ANC over the ten years, many showing ANC minima during 1990-1992, and maxima during 1995-1996. This is believed to be linked to the decadal-scale climatic cycles referred to above, which are discussed in detail in Section 5.3.3. As for alkalinity and pH, few sites show evidence of an overall trend in ANC, perhaps the most compelling being a decline in ANC at Lochnagar, consistent with rising NO_3 and falling pH at this site.

Figure 5.4

Temporal trends in Acid Neutralising Capacity (ANC) (µeq l⁻¹) at UKAWMN sites (1988-1998)

Smoothed line represents LOESS curve (Section 3.1.2)
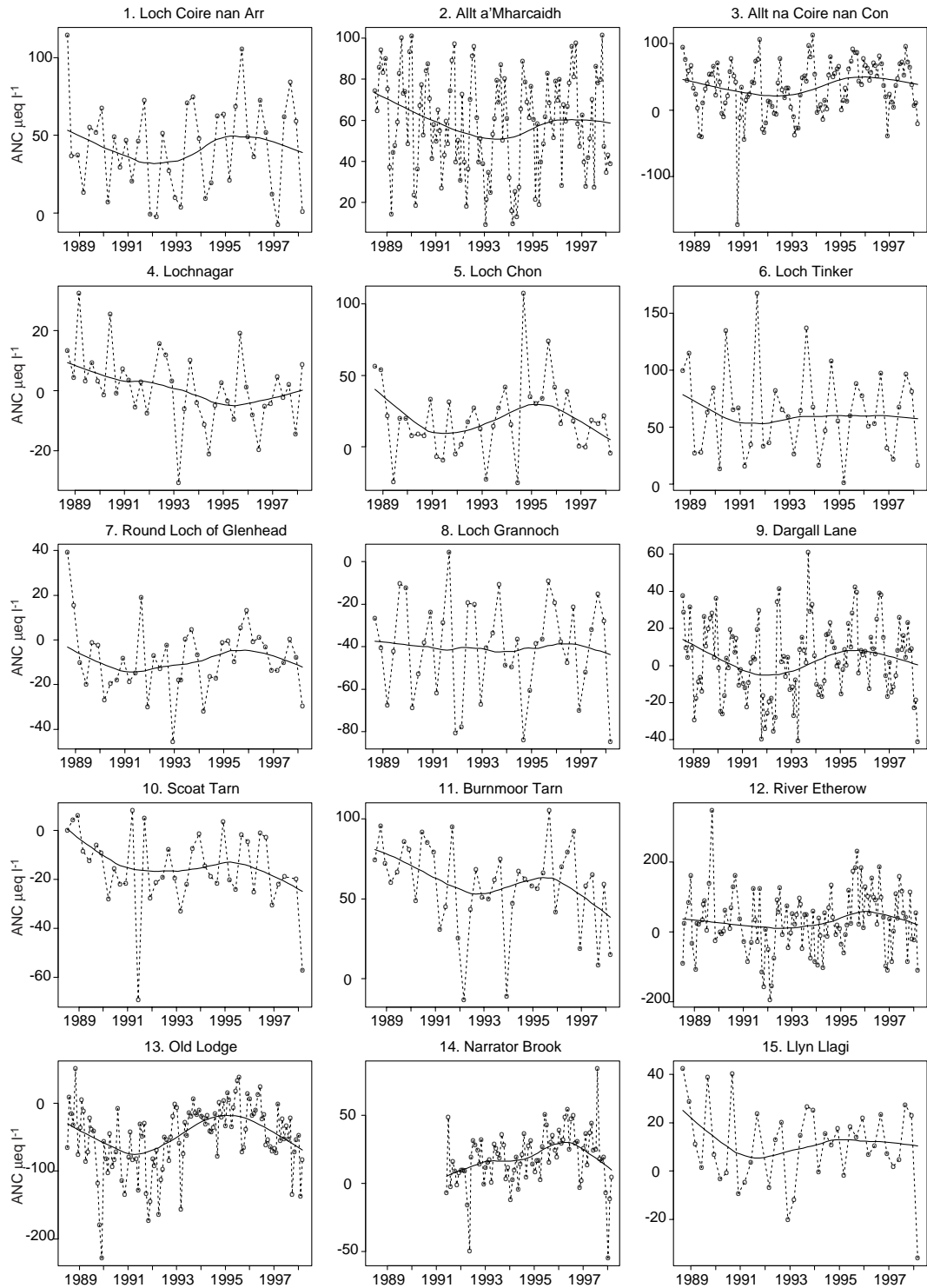
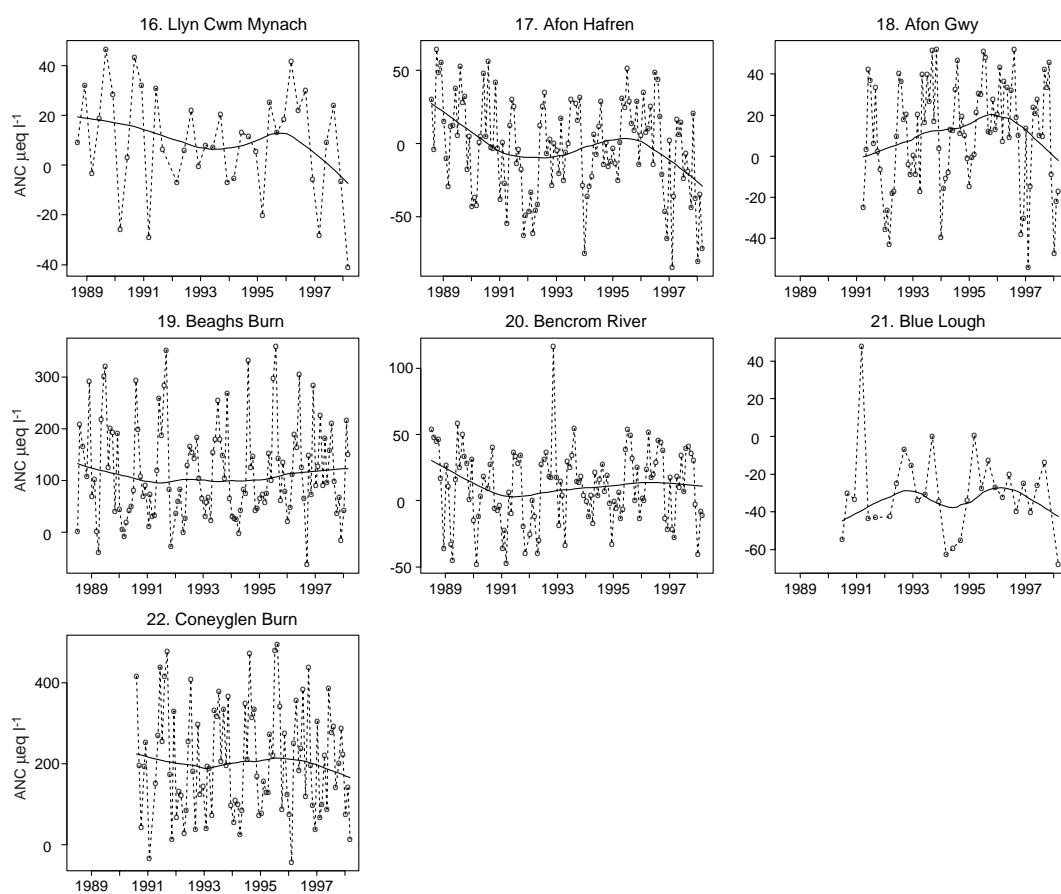# Figure 5.4 (continued)

Temporal trends in Acid Neutralising Capacity (ANC) (μeq l^{-1}) at UKAWMN sites (1988-1998)

5.2.2 Nitrate

Deposition of NO_3 and NH_4 has either remained stable or has risen slightly over the last decade (Chapter 2). Nitrogen saturation theory (Section 5.1.2) suggests that even a constant N input might be expected to lead to an increase in N output, and rising NO_3 trends have indeed been observed at six UKAWMN sites (Table 5.3). A rising trend is also suggested by time series data for Loch Grannoch (Figure 4.8.2e) but here and perhaps at others sites, any long term trend is difficult to detect amid large episodic and seasonal fluctuations. NO_3 is also thought to be affected by inter-annual climate variations; this is discussed in Section 5.4.

Of the six sites with rising NO_3 trends, the most compelling increases are at the River Etherow and Round Loch of Glenhead (Figures 4.12.2e and 4.7.2e), where steady changes over the ten years suggest increasingly severe catchment nitrogen saturation. Following apparent step changes at Lochnagar (in 1993, Figure 4.4.2e) and Loch Chon (in 1996, Figure 4.5.2e) concentrations have so far remained high, and again nitrogen saturation may be the cause. At Old Lodge, the 1991-1998 record is currently too short to confirm that changes have occurred, whilst at the Bencrom River (Figure 4.20.2e)

Table 5.3

Sites with increasing NO$_3$
SKT = Seasonal Kendall Test; REG = Linear regression.

| Site | NO$_3$ (µeq l^{-1}) | |
	SKT	REG
Lochnagar	*+1.4**	*+1.1**
Loch Chon	*+0.9**	*-*
Round Loch of Glenhead	*+0.9***	*+0.6**
River Etherow	*+2.1***	*+1.5**
Old Lodge	*+0.7**	*-*
Bencrom River	*+1.0**	*-*

* Trend significant at p < 0.05; ** trend significant at p < 0.01; *** trend significant at p < 0.001.

fluctuating concentrations over the monitoring period suggest that climatic factors may be the dominant influence.

5.2.3 Dissolved Organic Carbon

At 19 of the 22 sites in the Network, including all those in Scotland and Northern Ireland, rising DOC trends have been observed using one or both methods of trend analysis (Table 5.4). The only sites without observed DOC increases are Narrator Brook, Llyn Llagi and Llyn Cwm Mynach. Given the limited number of trends observed for other determinands, the consistency of the increases identified for DOC is remarkable, suggesting that concentrations may be rising in upland areas throughout most of the UK. At some sites these increases are extremely large; concentrations have doubled or more over the ten years at Loch Coire nan Arr, Allt na Coire nan Con, Dargall Lane, Scoat Tarn and Coneyglen Burn. Rising DOC trends have previously been noted at the Afon Hafren (1983-1993) by Robson & Neal (1996) and at the Afon Cyff and Afon Gwy (1980-1996) by Reynolds *et al*. (1997). Increase in water colour, which is strongly related to DOC concentration, has also been recorded at four Galloway lochs and three Trossachs streams between 1985 and 1995 (Harriman *et al*., 1995a) and in the Pennines between 1979 and 1998 (Naden & McDonald, 1989; Watts *et al*., in review).

The identification of widespread DOC increases at the UKAWMN sites raises three major questions. Firstly, do these trends represent a sustained, long-term increase in surface water DOC concentrations, or are they simply natural fluctuations? Secondly, what is the cause of observed changes? Finally, what, if any, are the biological implications of these changes?

(i) Validity of Trends

Time series data for sites exhibiting DOC trends generally suggest that these trends are 'genuine' (Figure 5.5). Unlike many other determinands there are few indications of cyclicity, with the majority of sites exhibiting steady, linear increases over time. This is reflected in the high level of SKT signficance at many sites (Table
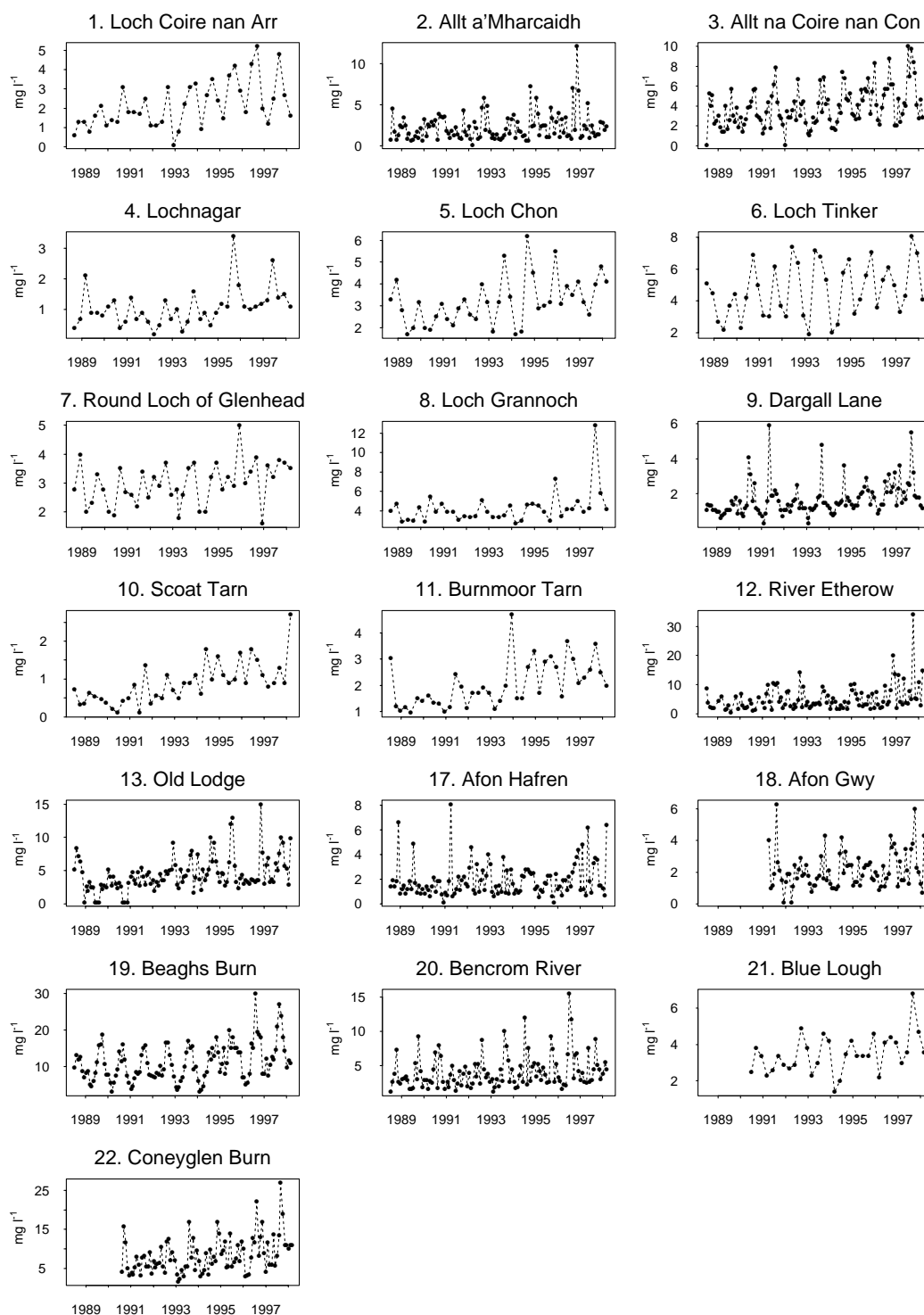
Figure 5.5

DOC at sites with rising trends

5.4) with increases at 12 sites significant at p <0.01. The analyses of Reynolds *et al*. (1997) and Robson & Neal (1996), showing similar increases for earlier time periods at the Gwy and Hafren, also support the conclusion that the changes observed in UKAWMN data form part of a sustained rising trend.

Interestingly, annual measurements of transparency (summer secchi disc depth) and the maximum depth of macrophyte growth (which is inversely correlated with DOC between sites) at UKAWMN lakes have not shown any apparent change over the last decade. This appears to suggest that increased DOC may not have led to an associated rise in colour in lake waters. Since the fraction of coloured compounds within the DOC total has been shown to vary (Molot & Dillon, 1997) it is therefore possible that observed DOC increases could have been in the low molecular-weight colourless forms. However, since colour is known to have increased in Galloway, the Trossachs and the Pennines (Harriman *et al*., 1995a; Watts *et al*., in review) and since there is evidence for an increase in absorbance at 250nm at some sites

Table 5.4

Sites with increasing DOC trends

| | DOC | | | | Non-labile Al | |
Site	SKT (mg l⁻¹)	REG (mg l⁻¹)	1st Year Mean (mg l⁻¹)	Annual % increase	SKT (µg l⁻¹)	REG (µg l⁻¹)
Loch Coire nan Arr	+0.25**	+0.21**	1.0	23%	+1.00*	+1.13**
Allt A'Mharcaidh	-	+0.11*	2.2	5%	-	-
Coire nan Con	+0.28**	+0.28**	2.8	10%	+2.40	+0.215
Lochnagar	-	+0.08*	1.1	8%	-	-
Loch Chon	+0.20**	+0.16**	3.4	5%	-	-
Loch Tinker	+0.18*	-	4.1	5%	-	-
Round Loch	+0.13**	+0.09*	2.9	4%	+2.31	+1.94**
Loch Grannoch	+0.13*	-	3.9	3%	-	-
Dargall Lane	+0.10**	+0.11**	1.1	10%	+0.86*	-
Scoat Tarn	+0.10**	+0.12**	0.5	22%	-	-
Burnmoor Tarn	+0.18**	+0.17**	1.6	11%	+0.25*	-
River Etherow	+0.27*	+0.48**	4.2	9%	+5.00**	+4.27*
Old Lodge	+0.28**	+0.35**	4.4	7%	-	-
Afon Hafren	+0.07*	-	2.1	3%	-	-
Afon Gwy	+0.10*	-	2.2	5%	-	-
Beagh's Burn	+0.60**	+0.65**	9.5	7%	-	-
Bencrom River	+0.14**	+0.21**	3.3	5%	-	-
Blue Lough	+0.19*	+0.18*	3.0	6%	-	-
Coneyglen Burn	+0.78***	+0.80**	6.4	12%	+1.86*	+2.42*

SKT = Seasonal Kendall Test.   REG = Linear regression.

First year mean calculated using data for April 1991-March 1992 at Afon Gwy, Blue Lough and Coneyglen Burn, April 1988-March 1989 at all other sites. Annual percentage increase calculated using mean of SKT and regression trend estimates where both are significant.

* indicates trend significant at p < 0.05, ** p < 0.01, *** p < 0.001.

(Harriman, pers. comm), it is possible that the observations above may reflect measurement limitations. This issue could be addressed in future by partitioning DOC in water samples by molecular weight using ultra-filtration, by measuring absorbance at a number of wave lengths, and or, by increasing the frequency of secchi disc readings.

(ii) Possible Causes of Rising DOC

At this stage, it is difficult to identify a mechanism for observed DOC increases. Krug & Frink (1983) argued that increasing mineral acid inputs to soils would cause a decrease in organic acid leaching, and hence in the DOC concentration of surface waters. This hypothesis was supported by palaeolimnological data showing a decline in DOC concentrations of Norwegian lakes concurrent with acidification during the early twentieth century (Davis *et al.*,1985). Modelling work by Tipping & Hurley (1988) suggested that with reductions in acid deposition, rising soil pH will lead to increased organic matter solubility, and hence to greater DOC in runoff. It is possible therefore that reduced acid deposition at UKAWMN sites over the last decade may be responsible for the rising DOC trends observed. However, this mechanism does not accord well with the geographical distribution of rising trends, as some of the largest increases have been at sites in low deposition areas, notably Loch Coire nan Arr, Allt na Coire nan Con, Beagh's Burn and Coneyglen Burn (Table 5.4). Since these sites have never been seriously acidified, it is unlikely that changing soil pH could be influencing DOC.

An alternative explanation for the observed trends may be a climatically driven increase in rates of organic matter decomposition. The steady increase in DOC identified for 1983-1993 at the Afon Hafren observed by Robson & Neal (1996) is accompanied by similar increases in Iodide (I) and Bromide (Br). Neal *et al*. (1990) note that both halogens are strongly influenced by microbial processes, with autumn stream maxima associated with peaks in the decomposition and washout of organic material. The rising trends in I and Br observed at the Hafren were therefore considered by Robson &

Neal (1996) to indicate a decomposition source for DOC increases. However, interactions between microbial organic matter decomposition and climate are complex. For instance, Christ & David (1996) found higher DOC production in a forest organic horizon with increased moisture content, while Mitchell & McDonald (1992) observed elevated concentrations for extended periods following droughts. Decomposition rates also increase exponentially with rising temperature (Christ & David, 1996).

Data presented by Marsh (1999) indicate an increased frequency of low flow conditions (and hence dryer soils) in southeast Britain during the last decade. No comparable trend has been observed in northwest Britain, and in general it is thought that rainfall patterns may be too spatially variable to account for consistent DOC trends throughout the UK. However mean temperatures show a much tighter spatial correlation, and data from the Central England Temperature Record (Hulme, 1999) indicate that the period 1988-1997 was on average 0.5°C warmer than the 1961-1990 mean. In addition, the average number of days with mean temperatures above 20°C during 1988-1997 (7.4 days yr^{-1}) was more than double the long term mean. Given the exponential relationship between decomposition and temperature, this apparent warming trend within the UK may be sufficient to explain the observed DOC increases. The increased number of hot summer days may be particularly significant since most decomposition can be expected to occur at these times.

(iii) Environmental Significance of Rising DOC.

Rising levels of DOC may have significant implications for stream and lake biota. The organic acids, which form part of the DOC, can have a significant negative impact on pH and alkalinity. Increases in organic acidity over the study period may therefore have reduced, or even negated, any recovery in pH and alkalinity resulting from reduced mineral acid anion concentrations. However, DOC has been shown to reduce fish mortality under acidic conditions, both through the complexation of toxic labile Al to non-labile forms and by reducing the toxicity of the remaining labile Al. (Baker *et al*., 1990;

Roy & Campbell, 1997). Since DOC supply is believed to be the limiting factor in non-labile Al generation (Driscoll *et al.*, 1984), this may explain the rising non-labile Al trends observed at seven sites with rising DOC (Table 5.4). Therefore, in terms of fish sensitivity to acidification, DOC increases may have a beneficial effect on UKAWMN surface waters.

Increases in water colour, although not yet identified at the UKAWMN lakes, will reduce the depth to which photosynthetically active radition penetrates, and as a result could restrict plant growth. High levels of colour are also considered to be a problem for drinking water (e.g. Mitchell & McDonald, 1992). Conversely, an increase in colour may provide aquatic organisms protection from the potentially harmful effects of UV-B radiation (e.g. Schindler *et al.*, 1996) which could be increasing in mid-latitudes as a result of stratospheric ozone depletion (e.g. Bjorn *et al.*, 1998).

■ 5.3 Impact of marine ion cycles on acidity and trend detection

5.3.1 Chloride Variations

Inter-annual variations in marine ion deposition, and subsequent cyclical fluctuations in surface water concentrations of a range of ions, have been examined in detail for eight UKAWMN lakes in the Trossachs, Galloway, the Lake District and north Wales by Evans *et al.* (in press). Figure 5.6 shows Cl time series and LOESS curves for these sites, along with Cl deposition for nearby monitoring sites. In all four regions, a peak in lake concentrations between 1989-1991 can be directly linked to elevated deposition inputs over the same period. An additional period of high Cl concentration at the Trossachs sites during 1993 corresponds to a second deposition peak in this region. Sea-salt deposition is in general highly episodic, with most inputs occurring during winter frontal storms. However, Reynolds & Pomeroy (1988) showed that physical mixing within the catchment damps surface water Cl response. Consequently, although significant seasonality is

evident in the time series shown in Figure 5.6, concentrations may remain elevated over sustained periods.

The patterns of surface water Cl variation observed at the sites studied by Evans *et al.* (in press) are mirrored at other west coast sites on the UK mainland. As noted in the site descriptions (Chapter 4), Dargall Lane, the Afon Hafren, Afon Gwy and Narrator Brook show virtually identical patterns of Cl variation to those observed in the Galloway, Lake District and north Wales lakes, with concentration maxima during the early 1990s (Figures 4.9.2f, 4.14.2f, 4.17.2f and 4.18.2f). This suggests that coastal areas ranging from southwest England to southwest Scotland have experienced very similar patterns of sea-salt deposition over the last decade. A period of high Cl concentration at Old Lodge during 1989-1991 (Figure 4.13.2f) suggests that this may also have extended along the English south coast.

Observed patterns of Cl variation for the Trossachs lochs are matched by those at the coastal sites in northern Scotland, Loch Coire nan Arr and Allt na Coire nan Con, and to some extent also by the inland sites, the Allt a'Mharcaidh and Lochnagar (Figures 4.1.2f-4.4.2f). These sites all exhibited elevated concentrations during 1989-1990 and 1993, indicating that both high deposition periods recorded in the Trossachs affected a wider area of northern Scotland. Cl variations at the Northern Ireland sites (Figures 4.19.2f-4.22.2f) are less consistent, perhaps reflecting their varied positions relative to coastlines, although concentrations appeared generally higher during 1990-1991 and 1995-1996.

5.3.2 Cations and Acidity

While deposited Cl is considered to be conservative within the catchment, accompanying cations have been shown to undergo chemical reactions through the 'sea-salt effect' (Wright *et al.*, 1988; Langan, 1989). High soil water concentrations of marine cations, primarily Na and Mg, cause displacement of other cations held on the soil exchange complex, which are then leached to surface waters. Na and Mg are in turn displaced as soil water
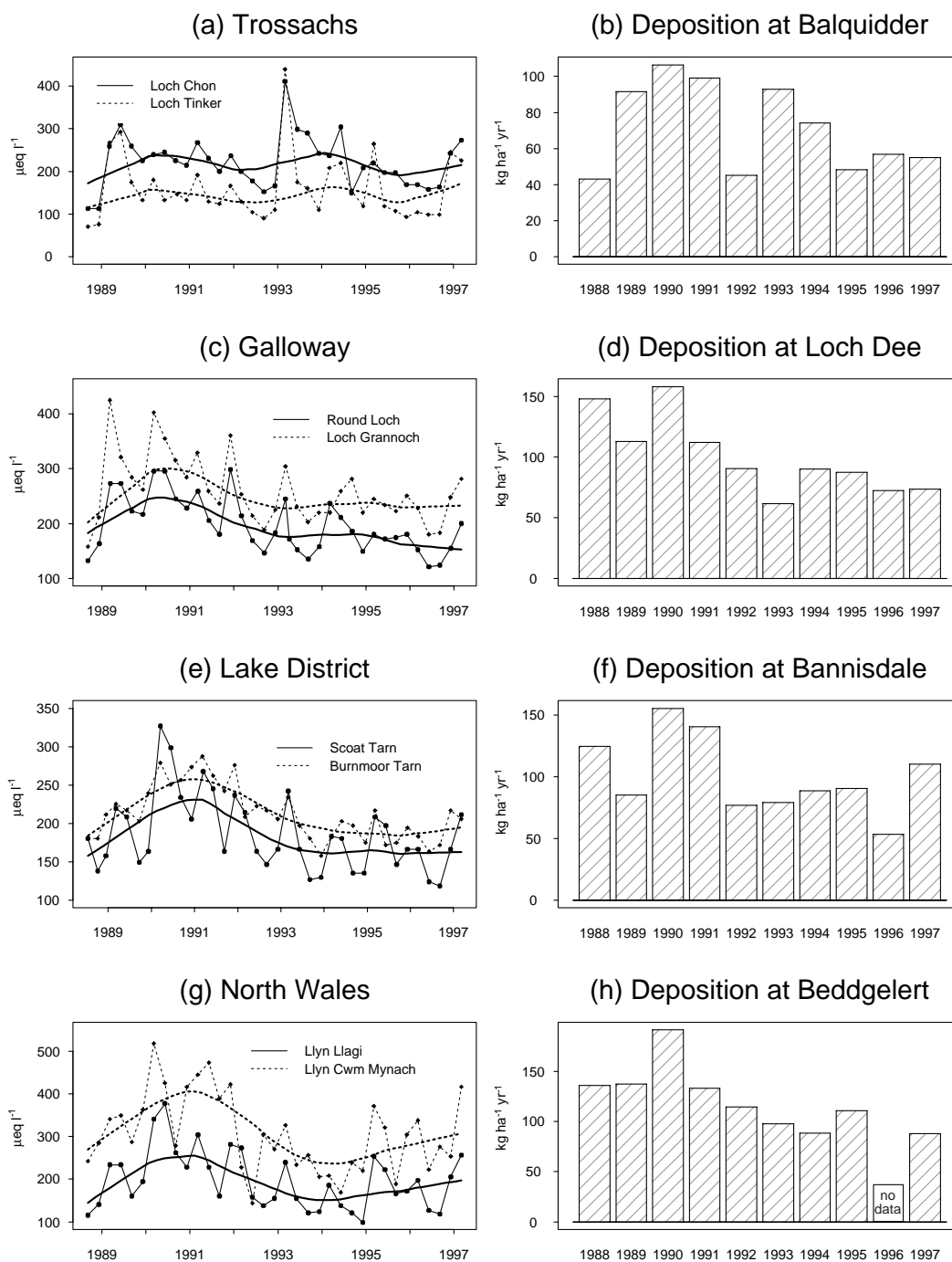
(a) Trossachs

(b) Deposition at Balquidder

(c) Galloway

(d) Deposition at Loch Dee

(e) Lake District

(f) Deposition at Bannisdale

(g) North Wales

(h) Deposition at Beddgelert

Figure 5.6

**Left) Cl time series for four geographical pairs of UKAWMN lakes (µeq l-1)
Right) Estimated annual Cl flux measured at local deposition monitoring station (kg ha-1 yr-1)**

concentrations return to pre-event levels, giving no overall change in the long term in either soil or surface water composition. Previous studies have in general considered the sea-salt effect as a transient process, focusing on episodic acidification due to H^+ displacement, but other cations with non-marine sources, notably Ca^{2+} and labile Al, may also be affected. Additionally, the sustained periods of elevated Cl observed at many UKAWMN sites suggest that the effects of soil ion exchange on runoff composition, may persist over much longer timescales than has previously been envisaged.

The influence of sea-salt inputs on surface water chemistry was assessed through linear regression between Cl (as a chemically inert indicator of marine inputs) and a range of potentially affected variables: xNa, xMg, xCa, H^+, labile Al and xSO_4. A negative correlation between the non-marine component of an ion and Cl suggests that this ion is adsorbed in the soil during periods of high sea-salt inputs, a positive correlation that it is displaced. For interpretation, sites were split into three categories based on the suggestion of Harriman *et al.*, (in press) that sites at an intermediate distance from the coast, with

Table 5.5

Slope and significance of regressions between Cl and a range of non-marine variables.

	xNa	xMg	xCa	H^+	Al_{lab}	xSO_4
'COASTAL' SITES						
Loch Coire nan Arr	-0.22***	-	-	+0.002***	-	-0.05***
Allt na Coire nan Con	-0.28***	-0.03***	+0.04***	+0.01***	+0.08***	-0.06***
Beagh's Burn	-0.37***	-	-	-	+0.05***	-
'INTERMEDIATE' SITES						
Loch Chon	-0.27***	-0.12***	-	+0.02***	+0.16***	-0.06*
Loch Tinker	-0.25***	-0.10***	-	+0.01***	-	-0.08*
Round Loch of Glenhead	-0.19***	-0.07*	-	+0.02*	+0.31***	-
Loch Grannoch	-0.27***	-0.08***	+0.05**	-	+0.89**	-
Dargall Lane	-0.26***	-0.02*	+0.08***	+0.02***	+0.23***	-0.05**
Scoat Tarn	-0.21***	-0.04*	+0.05***	+0.03*	+0.93***	-0.09***
Burnmoor Tarn	-0.23***	-	+0.21**	-	-	-
Old Lodge	-0.24***	-	+0.13***	-	-	-
Narrator Brook	-0.49***	-0.07***	-	+0.03***	+0.34***	-0.12***
Llyn Llagi	-0.21***	-0.07***	+0.07**	+0.03***	-	-0.07**
Llyn Cwm Mynach	-0.19***	-0.05***	+0.15***	-	-	-0.06*
Afon Hafren	-0.34***	-0.10***	-	+0.09***	+1.24***	-
Afon Gwy	-0.33***	-	-	+0.04*	+0.52**	-
Bencrom River	-0.26***	-	+0.10***	-	+0.29*	-
Blue Lough	-0.16**	-	-	-	+0.64*	-
Coneyglen Burn	-0.38***	-	-	+0.02**	-	-
'INLAND' SITES						
Allt a'Mharcaidh	-0.04***	-0.10***	-	+0.02***	+0.1*	-0.04*
Lochnagar	-	-	+0.11***	-	+0.6**	-
River Etherow	-	-	+0.13**	-	-	-

*All variables analysed in µeq l⁻¹ except labile Aluminium (Al_{lab}) (µg l⁻¹). *** indicates correlation significant at p < 0.001, ** significant at p < 0.01, *significant at p < 0.05. Correlations with p > 0.05 considered non-significant and omitted from table.*

generally moderate marine ion concentrations but receiving occasional large sea-salt inputs, undergo the most severe sea-salt acidification. At sites further inland sea-salt episodes are rare and generally minor, whereas in exposed coastal areas sea-salt deposition is continuously high, leading to proportionally small concentration changes in response to individual events, and therefore minor changes in acidity. Sites were classified on the basis of location and Cl concentrations as follows:

- 'Coastal': Very high Cl deposition. Maximum runoff concentrations > 600 µeq l^{-1} with large peaks during most years.
- 'Intermediate': Moderately high Cl deposition, maximum runoff concentrations commonly in range 350-500 µeq l^{-1}. Large inter-annual variations in deposition leading to cyclical variations in runoff Cl.
- 'Inland': Low Cl deposition, maximum runoff concentrations generally < 300 µeq l^{-1}. Some inter-annual variability but magnitude of changes insufficient to produce major sea-salt episodes.

In practice, the majority of acid-sensitive regions of the UK are in 'intermediate' locations, and this is reflected in the classification of UKAWMN sites. Only Loch Coire nan Arr, Allt na Coire nan Con and Beagh's Burn can be classified as 'coastal', whilst only the Allt a'Mharcaidh, Lochnagar and the River Etherow are 'inland'(high Cl concentrations at the Etherow are probably due to road salt, as noted in Section 4.12). Classifications and results of regression analyses are shown in Table 5.5, and some example time series in Figures 5.8-5.12.

Relationships between Cl and non-marine cations are generally consistent between sites. At all coastal and intermediate sites, xNa exhibits a highly significant inverse correlation with Cl, with slopes ranging from -0.16 to -0.49. These strong correlations indicate that marine Na is consistently retained on exchange sites following large sea-salt inputs. This effectively reduces the calculated xNa of runoff, and frequently results in a value below zero. Significant inverse correlations between xMg and Cl at 11 sites

demonstrate an equivalent process for marine Mg. The lower number of sites showing this relationship, and the smaller slopes observed, reflect the smaller amount of Mg in sea-salt relative to Na, and the proportionally greater non-marine Mg sources at some sites. Of the inland sites, the Allt a'Mharcaidh shows a similar inverse correlation for xNa and xMg to more marine-influenced sites, but the slope of -0.04 for xNa is much lower than elsewhere. At Lochnagar and the River Etherow no significant relationship is observed between Cl and either xNa or xMg, confirming that these sites are minimally influenced by sea-salt inputs.

Relationships between Cl and xCa, H^+ and labile Al, where observed, are invariably positive. In addition, at least one of these variables is significantly correlated with Cl at every coastal and intermediate site. Therefore, as would be expected, it appears that the retention of Na and Mg on exchange sites during sea-salt events is always accompanied by the displacement of one or more of Ca, H^+ and labile Al. However, the specific responses of individual catchments vary considerably. At Burnmoor Tarn, Old Lodge and Llyn Cwm Mynach, regression analyses suggest that only Ca is significantly displaced by Na and Mg inputs. At many other sites (e.g. Loch Chon, Round Loch, Narrator Brook, Afon Hafren, Afon Gwy) only the acid cations H^+ and labile Al appear to respond to sea-salts, whereas at Allt na Coire nan Con, Dargall Lane and Scoat Tarn all three cations are correlated with Cl. Therefore, although sea-salt effects operate at all these sites, the impact on surface water acidity may be minor at some and severe at others. The behaviour of individual catchments is not well related to site acidity, with for example both the acidic Old Lodge and circumneutral Burnmoor Tarn dominated by Ca displacement, although Table 5.5 does suggest some regional consistency in the response observed. It seems likely that local factors such as weathering supply and the nature of the exchange complex may determine specific cation response to sea-salt inputs.

It is important to note that the strength of the relationship between Cl and acidity cannot solely be attributed to marine ion effects. Major storm events, during which most sea-salt is deposited,

coincide to some extent with periods of high rainfall, when the contribution of relatively alkaline base-flow to surface waters can be diluted by surface runoff. Further work is therefore required to ascertain the relative influence of these two processes on inter-annual variation in acidity. Finally, it is worth noting that although all three coastal sites do show some displacement of non-marine cations by sea-salts, the slopes associated with the correlations in Table 5.5 are generally lower than at the intermediate sites. This appears to be consistent with the suggestion of Harriman *et al.* (in press) that acidification by sea-salts is less severe at sites experiencing very large and frequent deposition inputs.

5.3.3 Sulphate

Correlations between xSO_4 and Cl, included in Table 5.5, are significant at 10 of the UKAWMN sites. In all cases this relationship is negative, with slopes ranging from -0.04 to -0.12. The existence of a correlation between xSO_4 and Cl is surprising, since marine SO_4 is often considered to pass conservatively through the catchment. However Evans *et al.* (in press) have proposed a mechanism by which the elevated concentrations associated with large sea-salt inputs could cause temporary SO_4 retention. Unlike cation exchange processes, which occur mainly on organic matter in surface horizons, sulphate adsorption takes place on sesquioxides produced by weathering in

Figure 5.7

Hypothetical model of the influence of varying sea-salt deposition on SO_4 adsorbtion/ desorbtion within catchments and on marine/non-marine estimates from surface water samples
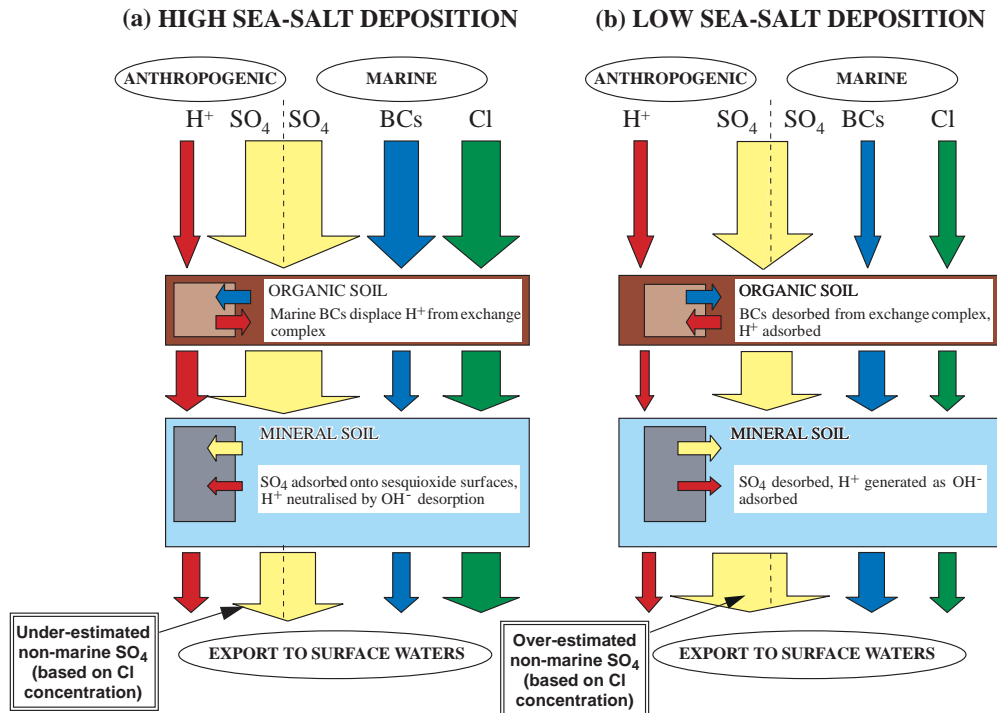
BCs = base cations. Arrow widths represent relative concentrations of specific ions as they pass from the atmosphere, through the soil profile and into the surface water. Only the concentration of conservative Cl remains relatively constant along the pathway. The use of fixed marine Cl:SO_4 and Cl:base cation ratios to estimate marine/non-marine fractions, leads to inevitable errors.

mineral soils, notably podzolic B horizons. The two processes are thus separated within the soil profile, and can be considered to operate in sequence as water percolates downwards. As water rich in marine ions passes through the soil, 'sea-salt' cation exchange processes occur first, leaving water entering the mineral soil enriched in both marine-derived SO_4 and H^+. Although most soils in the UK are believed to be fully saturated with SO_4 in the long term (Jenkins *et al*., 1997a) adsorption capacity is a function of concentration, and also of acidity, which increases the positive charge of sesquioxide surfaces (Johnson & Cole, 1980; Curtin & Seyers, 1990; Harriman *et al*., 1995b). Therefore, water rich in SO_4 and H^+ passing through the mineral soil during sea-salt events may temporarily increase adsorption capacity, leading to retention of some marine SO_4. Since adsorbed SO_4 is replaced in the soil water by desorbed OH^-, the impact of this will be to partially offset the episodic acidification generated by cation exchange processes. The proposed mechanism is illustrated in Figure 5.7.

A hypothesis of SO_4 retention during sea-salt events is supported by the observed inverse correlations between xSO_4 and Cl, and also by observations of individual episodes. During the large January 1998 sea-salt episode at Narrator Brook, for example (Figure 4.14.2), Cl rose from 250 to 480 µeq l^{-1} but total SO_4 remained constant. This implies that virtually all incoming marine SO_4 was adsorbed by catchment soils, leading to an observed fall in xSO_4 from 51 to 23 µeq l^{-1}. At the coastal Loch Coire nan Arr and Allt na Coire nan Con, xSO_4 levels have been observed to fall below zero during sea-salt events, and sea-salt episode data presented by Harriman *et al*. (1995b) for a range of Scottish streams show a similar pattern of xSO_4 decrease leading to the peak of a sea-salt episode. Finally, many of the UKAWMN sites exhibit generally opposing long term cyclicity in Cl and xSO_4 concentrations (e.g. Figures 5.8, 5.10, 5.11, 5.12), consistent with the operation of a SO_4 adsorption/desorption mechanism over a prolonged timescale. This is discussed further below.

5.3.4 Timescale and significance for trend detection

Although the sea-salt effect is generally considered to operate on an episodic timescale, it has already been noted that Cl concentrations have remained elevated for prolonged periods at many sites, resulting in widely observed, long term cyclicity. Given the relationships established in Section 5.3.2, inter-annual cyclicity would therefore be expected in the non-marine cations, xNa, xMg, H^+ and labile Al. This is certainly the case for xNa, time series which are often virtually the inverse of those for Cl (e.g. Figures 5.8-5.12). For example, xNa values were continuously negative for a year or more during 1989-1990 at Lochs Chon and Grannoch, Round Loch of Glenhead, Llyn Llagi and Llyn Cwm Mynach, but continuously positive for comparable periods during 1996-1997, when Cl was generally low. Cyclical variations in xMg, xCa, H^+ and labile Al are also evident in a large number of time series, including the examples given in Figures 5.8-5.12. It appears therefore that soil water concentrations, and the associated cation exchange equilibria, adjust gradually over time to changes in marine ion deposition. This is consistent with previous observations of strongly damped soil water and runoff Cl variations at Plynlimon (Reynolds & Pomeroy, 1988) but has not previously been identified with regard to sea-salt effects on acidity.

Variations in xSO_4 also show clear cyclicity. This has already been noted in individual site descriptions (Chapter 4), with concentrations at many locations having risen following the 1990 Cl deposition peak until around 1994 (Figure 5.3). The five year analysis of UKAWMN data (Patrick *et al*., 1995) consequently identified rising xSO_4 trends at a number of sites, but Figure 5.3 suggests that since 1994 concentrations at most sites have fallen. Since deposition data for the same areas do not show comparable increases over the first half of the monitoring period (Chapter 2), it seems probable that the observed surface water xSO_4 cyclicity may have been driven by marine ion cycles, and resulting adsorption/desorption. Effectively the ratio between Cl and marine SO_4 in runoff fluctuates as the latter adsorbs and desorbs from

Figure 5.8

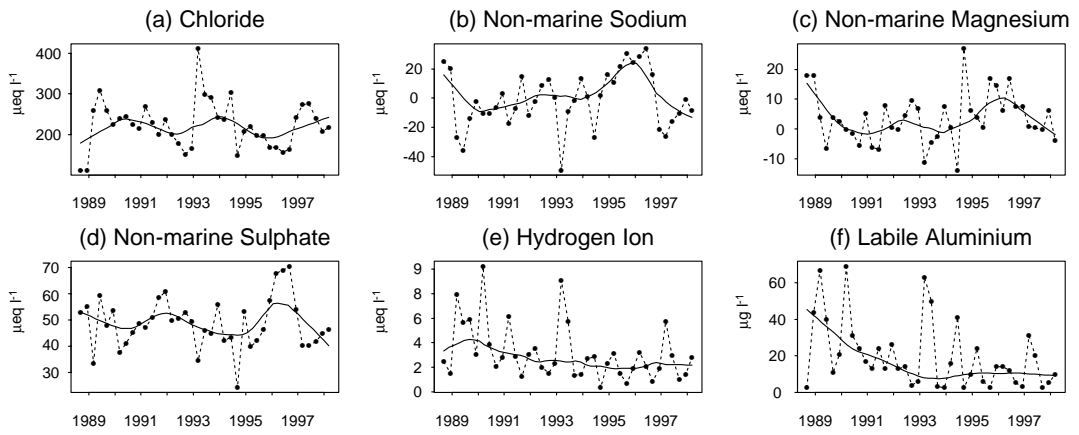**CI and correlated non-marine determinands, Loch Chon**

(a) Chloride

(b) Non-marine Sodium

(c) Non-marine Magnesium

(d) Non-marine Sulphate

(e) Hydrogen Ion

(f) Labile Aluminium

Figure 5.9

CI and correlated non-marine determinands, Round Loch of Glenhead

(a) Chloride

(b) Non-marine Sodium

(c) Non-marine Magnesium

(d) Hydrogen Ion

(e) Labile Aluminium
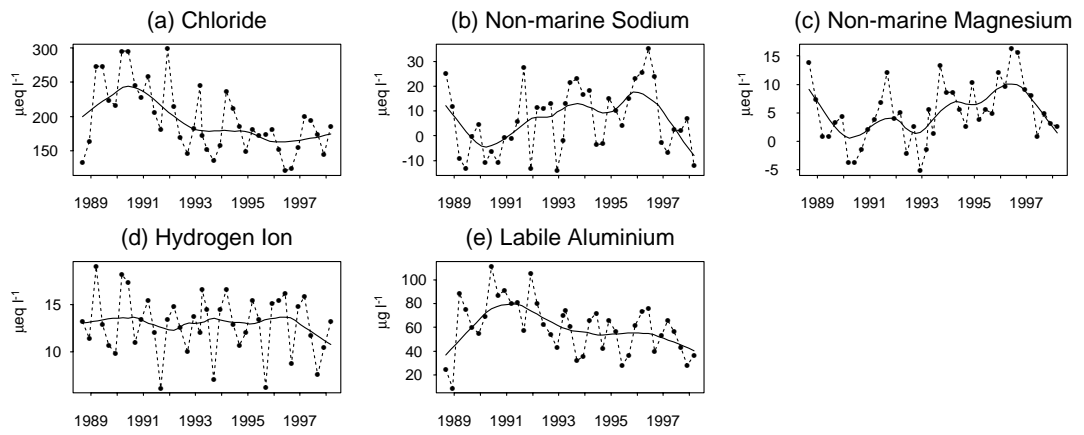
Figure 5.10

CI and correlated non-marine determinands, Scoat Tarn

(a) Chloride

(b) Non-marine Sodium

(c) Non-marine Magnesium

(d) Non-marine Sulphate

(e) Non-marine Calcium

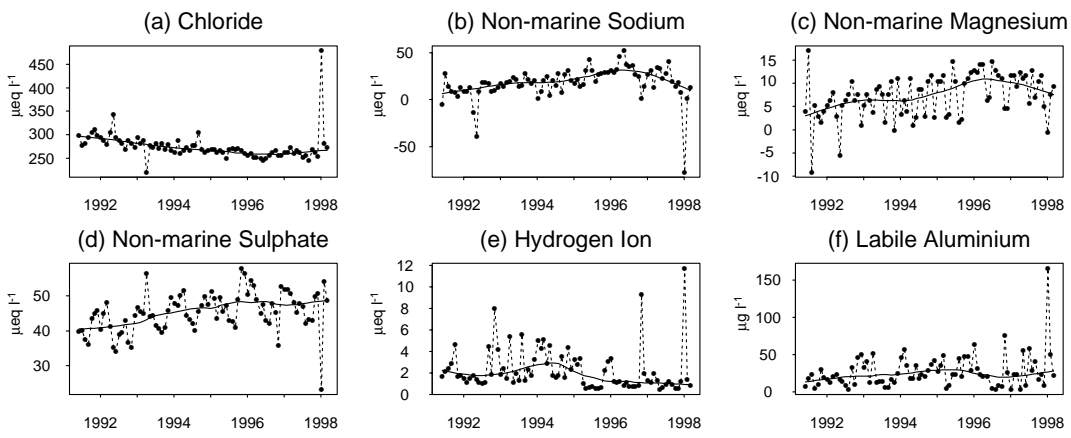(f) Hydrogen Ion

(g) Labile Aluminium
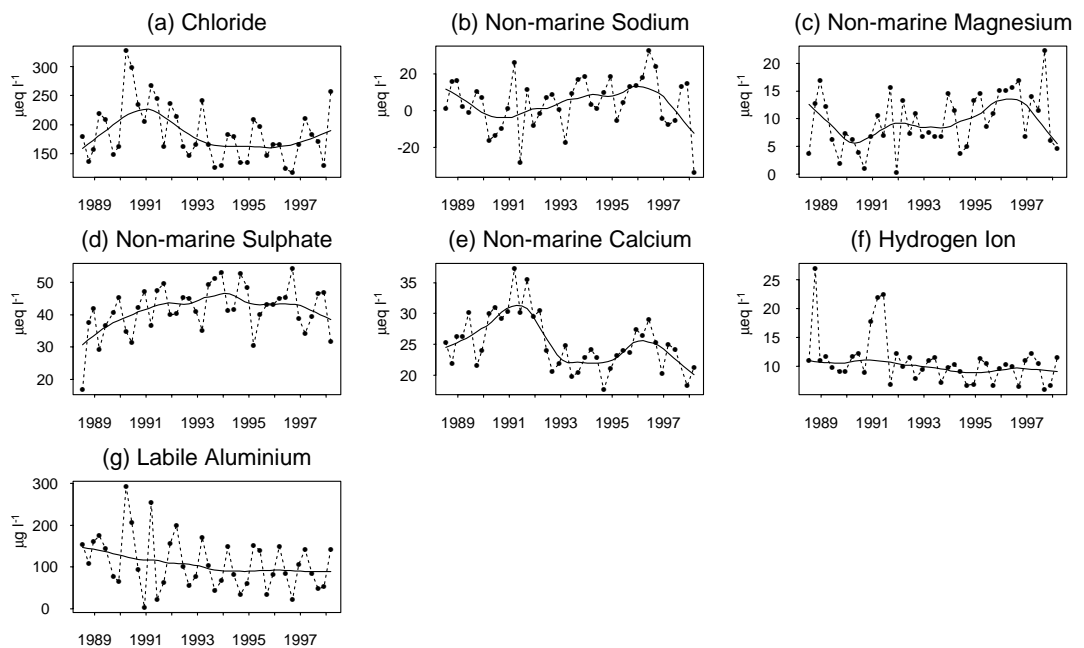
Figure 5.11

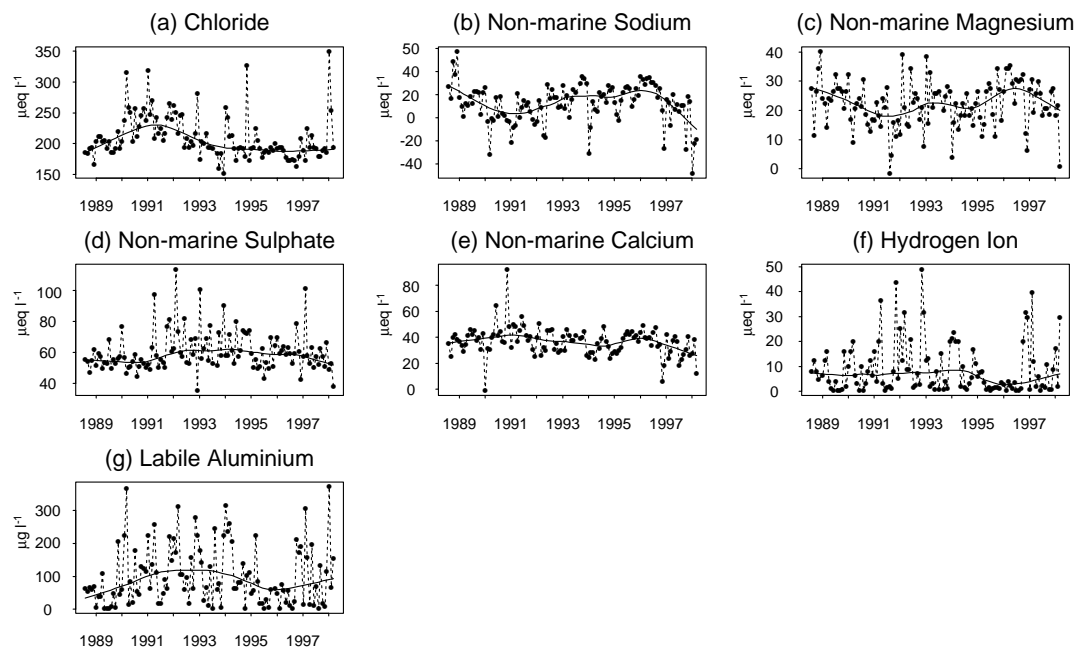**CI and correlated non-marine determinands, Narrator Brook**

Figure 5.12

CI and correlated non-marine determinands, Afon Hafren

the soil, leading to an error in the calculation of xSO_4 based on fixed sea-salt ratios (Figure 5.7).

Observations of the UKAWMN dataset suggest, then, that a large number of sites experience long term cyclicity in marine ion deposition, and consequently in surface water levels of chloride, base cations, sulphate, labile Al and acidity. Since this cyclicity appears to operate, in many cases, over a timescale at least as great as the ten years over which monitoring has been carried out, there are two major implications for trend detection.

First, there is the likelihood of identifying spurious trends using monotonic trend detection techniques. Robson & Neal (1996) gave an example in which seasonally varying data superimposed on a single sinusoidal cycle were mis-indentified as a significant trend using SKT. This problem has to a large degree been overcome in the present study through the use of LOESS curves to visually identify cyclicity in time series. However, the frequency with which both SKT and regression detected significant trends in Cl, Na, Mg and Ca, as noted in individual site descriptions, illustrate the need for caution in this respect. Apparent increases in pH and alkalinity at a number of sites were also linked to marine ion cycles rather than long term site recovery.

The second problem for trend analysis is that genuine, anthropogenically driven changes may be obscured by climatically driven fluctuations in marine ion deposition. In effect these can be considered sources of 'noise', along with flow and seasonally-related variations, but due to their duration climatic cycles are less easy to isolate without a longer dataset than that currently available. Although relatively few sites in the UKAWMN have exhibited clear xSO_4 decreases or pH/alkalinity increases, it is thought that underlying improvements may have been obscured by climatic factors, and that these may become apparent after further monitoring.

5.3.5 The North Atlantic Oscillation as a controlling mechanism

The North Atlantic Oscillation (NAO) has recently been recognised as an important influence on European climate (e.g. Hurrell, 1995; Rodwell *et al.*, 1999). North Atlantic weather systems are dominated by two 'centres of action', the Iceland Low and the Azores High, and the NAO Index (NAOI) is quantified as the difference in surface pressure between these two locations. Pressure gradients and inter-annual variability tend to be greatest during winter, leading to the most pronounced weather variations at this time. For the UK, winters characterised by high values for the NAOI, i.e., large pressure gradients, are associated with relatively warm, wet weather, dominated by strong southwesterly or westerly air flows. Occasional negative values represent a reversal of pressure systems, where blocking highs over Scandinavia or the northeastern Atlantic lead to colder winters dominated by northeasterly winds. Storms, and hence sea-salt deposition, tend to be most frequent during high NAO conditions. Conversely, low or negative NAO winters are associated with dry, cold conditions, and low sea-salt deposition. Unusually high winter NAOI values were recorded during the late 1980s and early 1990s, coinciding with the peak in surface water Cl concentrations at the majority of UKAWMN sites. Lower NAOI values in more recent years have coincided with lower observed Cl concentrations, and overall there appears to be a strong correlation between NAOI and Cl (Figure 5.13). The second Cl peak in northern Scotland during 1993 coincided with a brief period of high NAOI, but Lamb Weather Indices (Davies *et al.*, 1991) obtained from the Climatic Research Unit, University of East Anglia, show that this was associated primarily with westerly rather than southwesterly airflows. Sites further south on the UK mainland are thought to be partly sheltered from westerly storms by Ireland, and thus did not receive major sea-salt inputs at this time. This interpretation is supported by Cl peaks at the two coastal Northern Ireland sites, Beagh's Burn and Coneyglen Burn concurrent with those in northern Scotland (Figures 4.19.2f, 4.22.2f).

In recent decades the NAO has shown approximately decadal cyclicity. Although it appears that only one major NAO 'cycle' has occurred during the ten years of UKAWMN monitoring, an earlier high NAOI period was
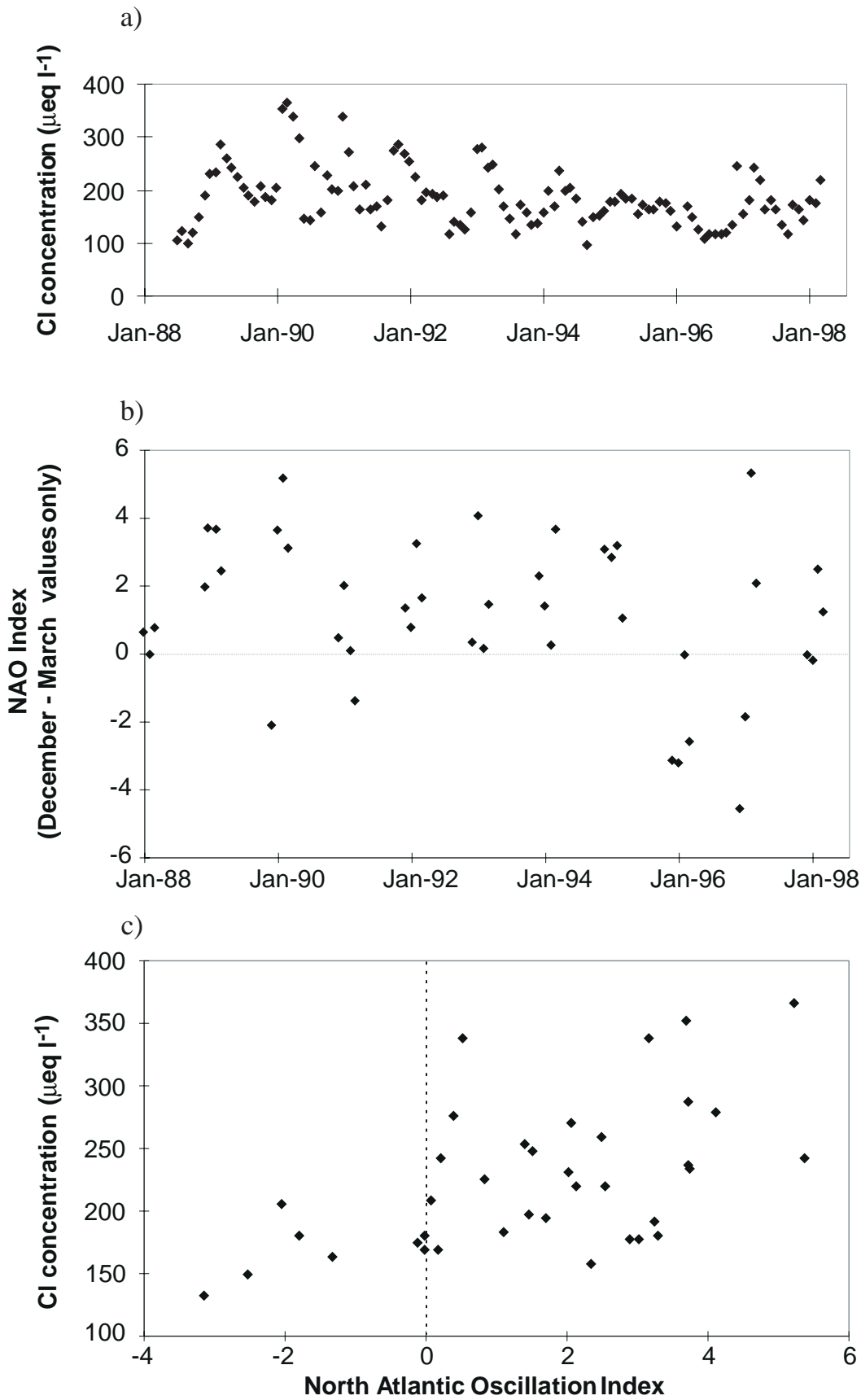
a)

b)

c)

Figure 5.13

a) Chloride concentration time series for Dargall Lane (1988 - 1998) b)Monthly North Atlantic Oscillation Index (NAOI) (December - March only) (1988 - 1998) c) Scatter plot of temporal relationship between Cl concentration at Dargall Lane and NAOI for the previous month. Data are for winter NAOI only (i.e. December - March)

recorded during 1983-1984. In Chapter 6, data are presented for five sites in Scotland and Wales where monitoring extends back to this period, and it appears that this NAOI peak was again accompanied by high Cl concentrations. These data also support an inverse relationship between xSO_4 and Cl over a longer time period.

5.3.6 Summary

Long term cyclicity in a wide range of surface water determinands has been observed at many of the UKAWMN sites, and can be linked to inter-annual variations in sea-salt deposition. It is thought that this variability in deposition is the result of natural climatic fluctuations, probably driven by the North Atlantic Oscillation. Changes in marine ion inputs affect surface water chemistry through the sea-salt effect, whereby marine-derived Na and Mg displace non-marine H+, labile Al and Ca from the soil. In most instances this leads to the transient acidification of runoff, although the relative extent to which individual non-marine cations are displaced appears to vary depending on catchment soil properties. There is also evidence to suggest that adsorbtion of SO_4 is enhanced during periods when sea-salt inputs are high, while desorbtion occurs when inputs are low. This transient soil retention and release of SO_4, in response to

climatic variations, has not previously been recognised as an influence on surface water chemistry. The major impacts appear to be that; (a) acid anion concentrations are reduced during high Cl periods, partially offsetting acidification caused by cation exchange processes; and (b) the ratio between marine SO_4 and Cl in runoff varies in time, generating an error in the calculation of non-marine SO_4 based on fixed sea-salt ratios.

Although the sea-salt effect has previously been thought of as an episodic process, the long term cyclicity observed in the UKAWMN data suggest that effects may be sustained over prolonged periods in the UK. The presence of climatically driven cyclicity in determinands such as pH and xSO_4 has important implications for trend detection in coastal regions of the UK and elsewhere, indicating that monitoring periods in excess of ten years are required in order to clearly identify the effects of anthropogenic emission changes on acid-sensitive surface waters.

■ 5.4 Climatic Influences on Nitrate Variations

Spatially, mean NO_3 concentrations in UKAWMN freshwaters show a positive relationship with N deposition (see Section

Figure 5.14

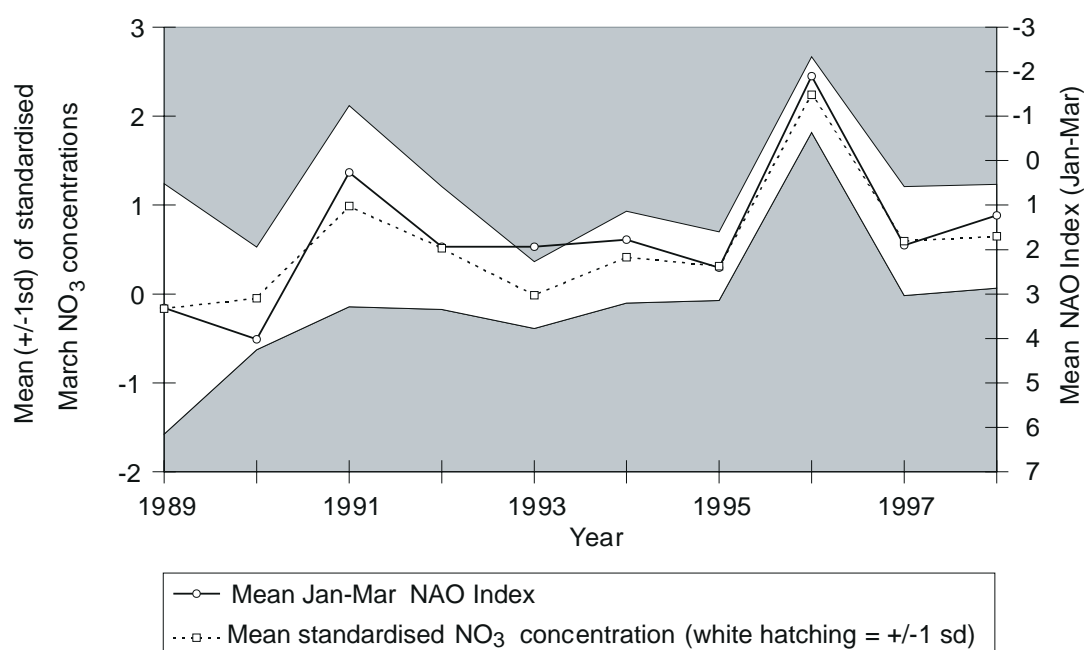**Variance in NO$_3$ concentration (standardised by the site mean) for 5 UKAWMN lakes (1988 -1998)**
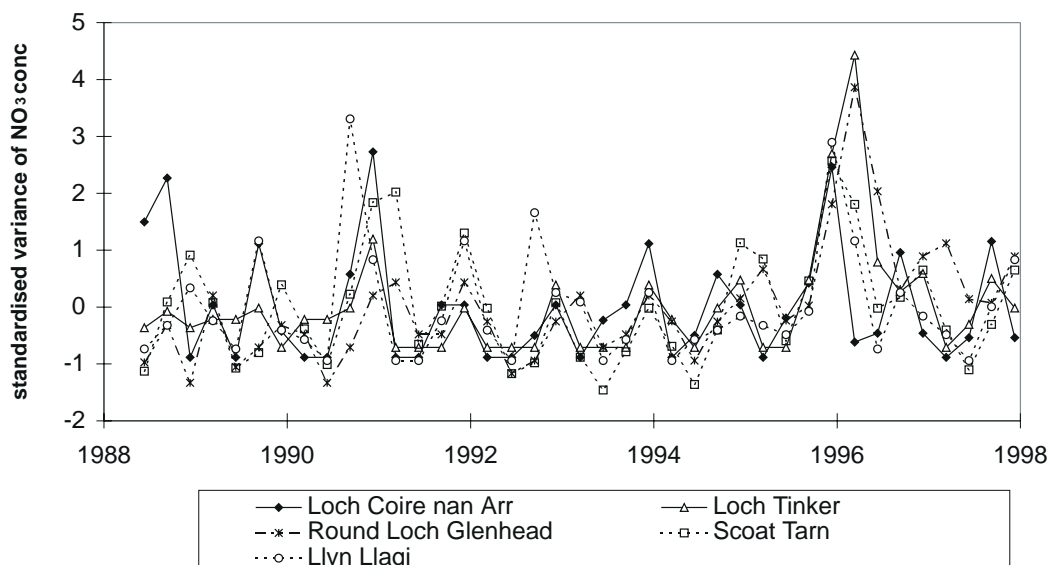
5.1.2). However, over the past decade, temporal variation in NO$_3$ concentration, often strongly correlated between sites, shows little relationship with temporal patterns in N deposition. NO$_3$ concentrations usually peak in the spring, and since lakes are only sampled quarterly, March samples from lakes tend to represent the annual maximum. Figure 5.14 demonstrates that for most lake sites, NO$_3$ concentrations were relatively high in the March samples of 1991 and 1996. NO$_3$ peaks at monthly sampled stream sites usually occur between December and March and again, for several sites, these peaks are relatively elevated in the springs of 1991 and 1996 (Figure 5.2).

Interannual variation in NO$_3$ concentration has been observed in a number of studies in recent years. Several climatic parameters have been proposed to explain this phenomenon, including summer drought (Reynolds *et al.*, 1992), summer temperature (Murdoch *et al.,* 1998) and winter freeze thaw (Mitchell *et al.*, 1996). Given the strong correlation between the NO$_3$ time series of most UKAWMN lakes, Monteith *et al.* (in press) adopted a meta-analysis approach (ie. reducing NO$_3$ time series for a group of sites to a single variable) to explore possible relationships between NO$_3$ concentration and climatic

variables. Rainfall time series were rejected as potential explanatory variables, since temporal variation in precipitation has been highly variable across the UK over the past decade. Analysis therefore focused on mean monthly air temperature, taken from the Central England Temperature Record (CET) (Hulme, 1999), which is highly correlated with air temperature records for sites across the UK, and the North Atlantic Oscillation Index (NAOI) (see section 5.3.5) which is increasingly being shown to represent variations in UK climate at the regional scale.

Similarity between UKAWMN lakes in NO$_3$ time series is demonstrated in Figure 5.14 which compares lake concentrations standardised by the site mean. Atypically, the seasonal NO$_3$ leaching pattern at Lochnagar changed abruptly in 1993 (section 4.4) and this site was removed from further analysis as a statistical outlier. Blue Lough was also removed due to the relatively short time series available. The mean of the standardised variance of March NO$_3$ concentration for the remaining nine lake sites was strongly and inversely correlated with the mean January to March NAOI (linear regression: $r^2 = 0.90$ $P < 0.0001$; Spearman Rank correlation: $r^2 = 0.85$ p<0.001)(Figure 5.15). The latter

correlation demonstrates that this relationship is not simply driven by a chance coincidence of extreme values for concentration and NAOI in two years (1991 and 1996). Winter temperature has been shown to be closely related to winter values for the NAO (Hurrel, 1995) and this relationship appears to link high NO_3 leaching with cold winters. Indeed, mean standardised March NO_3 is also significantly and inversely correlated with mean January to March CET (linear regression: $r^2 = 0.61$ $p<0.01$) and mean December to March CET (linear regression: $r^2 = 0.67$ $p<0.01$).

Similar relationships hold for UKAWMN stream sites although, given the greater between-site temporal variability in NO_3 concentration, a meta-analysis approach was deemed inappropriate. NO_3 time series for monthly sampled stream sites demonstrate how the timing of peak concentration varies between years. For several stream sites the strongest relationships with climatic variables were found between the annual peak NO_3 and mean December to March NAOI.

As an independent test of the NO_3:NAO relationship the authors also analysed the eighteen year record available for the Afon Gwy, which has been monitored as part of the Plynlimon experiment (Reynolds *et al.*, 1997). Again, the relationship between peak winter NO_3 and mean December to March NAOI was highly significant. Although the relationship appears to reflect an effect of low winter temperatures on high NO_3 leaching, the mechanism is as yet unclear. The correlation between on-site measured air temperature and NO_3 concentration in the longer Afon Gwy dataset is relatively weak. However a strong relationship was found between the number of days with grass minimum temperature $<=-4°$ c and peak winter NO_3 concentration. It is possible that for the Gwy catchment, this temperature is associated with a critical threshold for freezing in the upper soil horizons, which could have a biocidal effect on soil microbial biomass, and cause damage to plant roots and changes in soil organic matter. Thawing in spring could then make the resulting lysis products available for mineralisation, while low temperatures and frost damage to plants

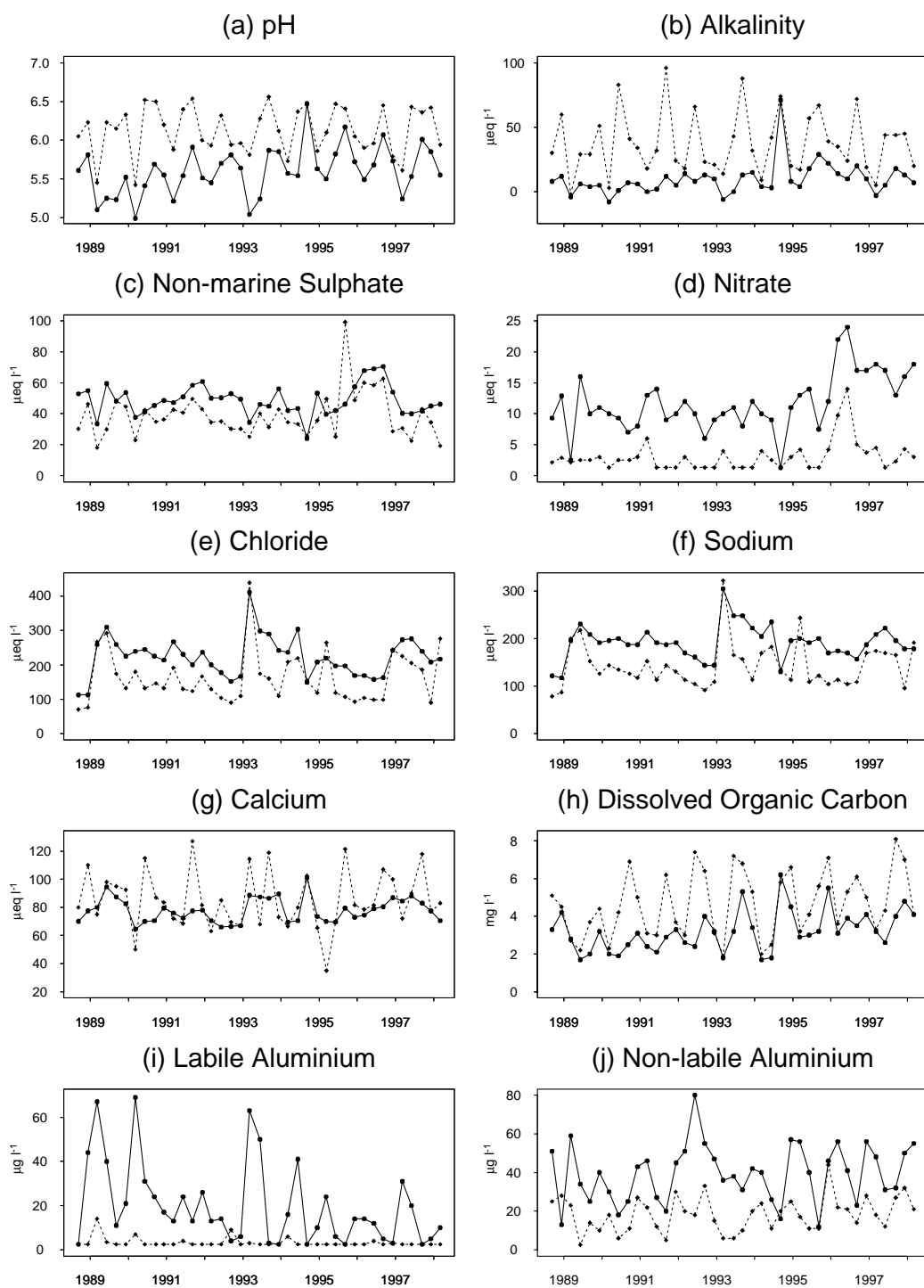might restrict terrestrial uptake, hence maximising potential leaching into freshwaters.

Further work is necessary to elucidate the precise nature of the link between NO_3 concentrations and the NAO. However, it would appear that NO_3 leaching from these systems is strongly influenced by a regional to global scale climatic process, and this has to be carefully considered when assessing temporal trends and their likely causes.

■ 5.5 Influence of Forestry on surface water chemistry

The UKAWMN contains three sets of 'paired' forest and moorland catchments. These are Loch Chon and Loch Tinker in the Trossachs (3 km apart), Loch Grannoch and Round Loch of Glenhead in Galloway (14 km), and the Afon Hafren and Afon Gwy in Mid Wales (3 km). Table 5.6 summarises catchment characteristics, and shows that geology and soils are largely similar for each pair. Differences do exist in the lake and catchment sizes of the two Scottish pairs, and in the altitude of the Trossachs pair, which may cause differences in surface water chemistry that are unrelated to forestry. Nevertheless all three pairs are felt to be sufficiently similar that a general assessment of forest impacts on runoff chemistry can be undertaken.

5.5.1 Loch Chon and Loch Tinker

The two Trossachs lochs drain adjacent catchments, with the same underlying geology. However Loch Chon is at lower altitude, has a larger catchment and lake area, and soils have a higher mineral content than at Loch Tinker. Mean chemistry data (Table 5.7) and time series (Figure 5.16) show substantial differences between the two lochs; Loch Chon is consistently more acidic, with higher acid anion and aluminium levels. Ca concentrations are similar, suggesting that differences in catchment base cation supply are not important, although higher DOC levels at Loch Tinker reflect the dominance of organic soils in this catchment. The higher xSO_4, NO_3 and Cl concentrations at Loch Chon are thought to result from enhanced dry and

(a) pH

(b) Alkalinity

(c) Non-marine Sulphate

(d) Nitrate

(e) Chloride

(f) Sodium

(g) Calcium

(h) Dissolved Organic Carbon

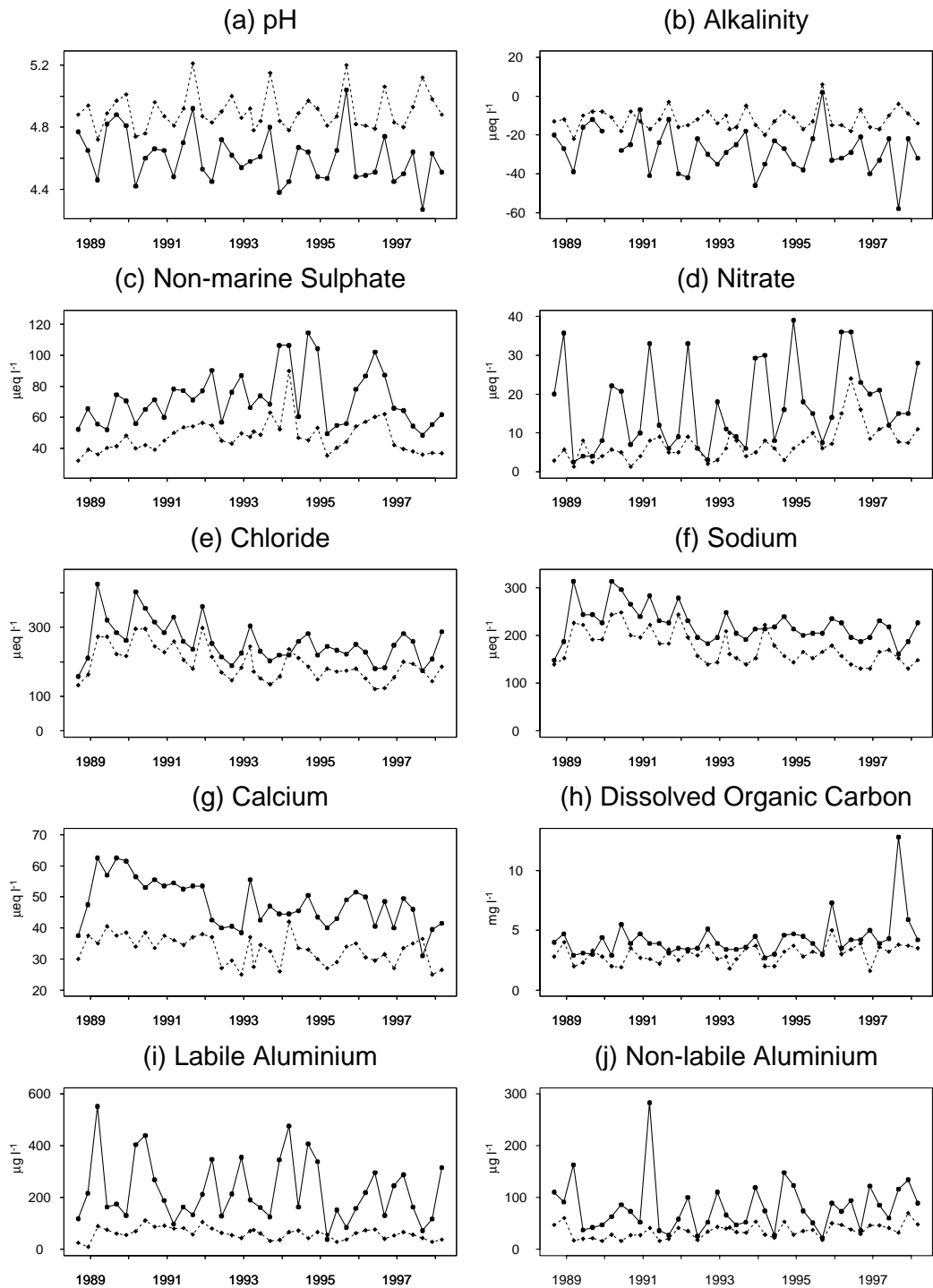## (i) Labile Aluminium

(j) Non-labile Aluminium

Solid line represents Loch Chon (forested), dashed line Loch Tinker (moorland)

Figure 5.17

Water chemistry time series for the forested : moorland pair, Loch Grannoch and Round Loch of Glenhead

(a) pH

(b) Alkalinity

(c) Non-marine Sulphate

(d) Nitrate

(e) Chloride

(f) Sodium

(g) Calcium

(h) Dissolved Organic Carbon

(i) Labile Aluminium

(j) Non-labile Aluminium

Solid line represents Loch Grannoch (forested), dashed line Round Loch of Glenhead (moorland)

Table 5.6

Characteristics of paired forested and moorland catchments

Site	Forest (%)	Geology	Soils	Min. Altitude (m)	Catchment Area (ha)	lake Area (ha)
Loch Chon	*44%*	*Mica schists and grits*	*Peaty gleys, peaty podzols*	*100*	*1570*	*100*
Loch Tinker	*0%*	*Mica schists and grits*	*Peat*	*420*	*112*	*11*
Loch Grannoch	*70%*	*Granite*	*Peat, peaty podzols, peaty gleys*	*210*	*1287*	*114*
Round Loch	*0%*	*Tonalite, granite*	*Peat, peaty podzols*	*295*	*95*	*13*
Afon Hafren	*50%*	*L. Paleozoic sedimentary*	*Peat, stagnopodzols*	*355*	*358*	*-*
Afon Gwy	*0%*	*L. Paleozoic sedimentary*	*Peat, stagnopodzols*	*440*	*210*	*-*

occult deposition of marine and pollutant ions to the forest canopy (Mayer & Ullrich, 1977). Mean NO_3 concentrations in particular are a factor of four times higher than at Loch Tinker, where the majority of samples are below detection limits (Figure 5.16d). NO_3 at Loch Chon only fell below detection limits once during the monitoring period, suggesting that afforestation has caused increased N leaching at this catchment. The combined impact of elevated xSO_4 and NO_3 at Loch Chon has been to cause significant additional acidification, with estimated reductions of 0.5 pH units and 14 µeq l^{-1} of alkalinity (Table 5.7), and a major associated increase in levels of labile Al. These conclusions are supported by a palaeolimnological study by Kreiser *et al.* (1990), which suggests that pH values dropped rapidly at Loch Chon following catchment afforestation in the 1950s, whilst pH at Loch Tinker remained relatively constant over the same period.

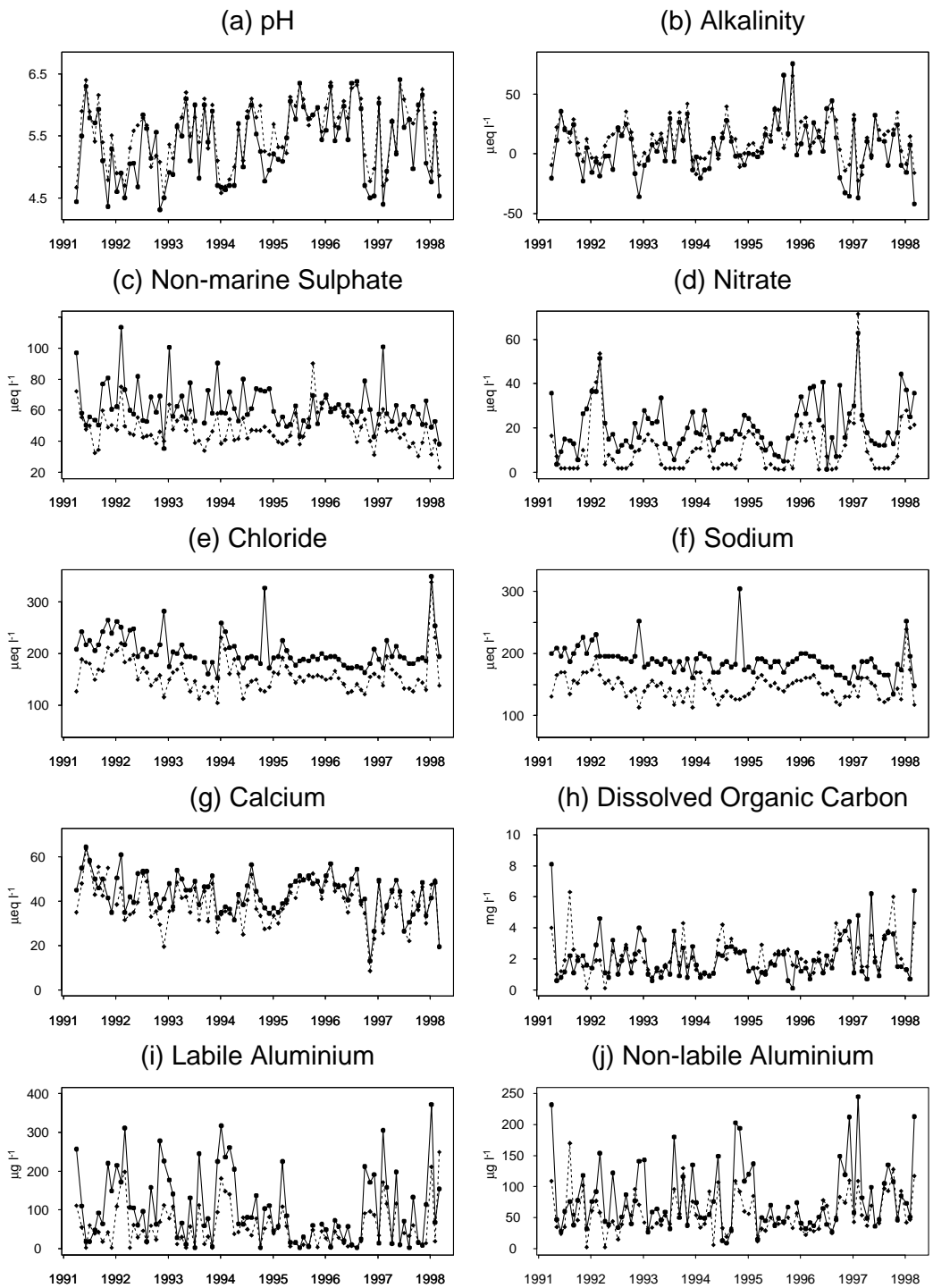### 5.5.2 Loch Grannoch and Round Loch of Glenhead

The Galloway lochs are generally comparable in terms of geology, soils and altitude, although Loch Grannoch has a larger lake and catchment area than Round Loch. Chemical differences between the two sites are very similar to those between Lochs Chon and Tinker, with xSO_4, NO_3 and Cl all higher at the forested Loch Grannoch (Table 5.7). Time series (Figure 5.17) indicate that higher xSO_4 and Cl levels are sustained throughout the year, whereas NO_3 concentrations are very similar to those at Round Loch during summer but rise to much higher peaks during winter. This suggests that elevated N inputs to Loch Grannoch are largely retained during the growing season, but washed out during the dormant season. Although both lochs are acidic, the higher pollutant anion concentrations at the forested site have led to consistently lower pH and alkalinity, and much higher labile Al. Higher Ca and Mg at Loch Grannoch may be due to displacement from the soil by incoming H^+, or simply to a greater weathering supply in this catchment.

A notable feature of time series data for the Galloway lochs is that, whereas the Round Loch may have shown a slight improvement in pH over the monitoring period, Loch Grannoch appears to have acidified further since 1988.

Figure 5.19

Water chemistry time series for the forested : moorland pair, Afon Hafren and Afon Gwy

(a) pH

(b) Alkalinity

(c) Non-marine Sulphate

(d) Nitrate

(e) Chloride

(f) Sodium

(g) Calcium

(h) Dissolved Organic Carbon

(i) Labile Aluminium

(j) Non-labile Aluminium

Solid line represents Afon Hafren (forested), dashed line Afon Gwy (moorland)
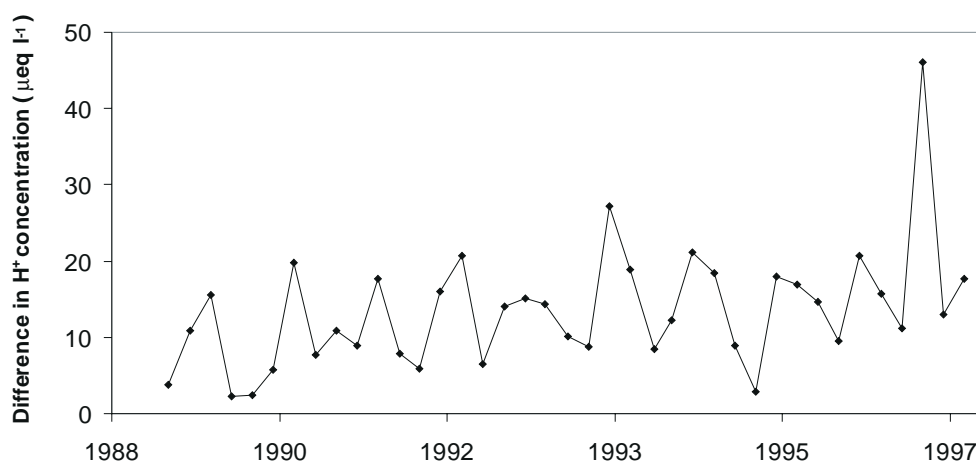
Neither trend was significant in the original trend analysis, but a Seasonal Kendall analysis of the difference in H^+ concentrations between sites shows a highly significant increase, of around 0.8 µeq l^{-1} H^+ per year (Figure 5.18). This supports the earlier suggestion that forestry at Loch Grannoch is causing a continued deterioration in water quality.

5.5.3 Afon Hafren and Afon Gwy

The Hafren and Gwy catchments are very similar in all respects other than land-use, and are therefore well suited to an assessment of forestry impacts. As in the Scottish catchment pairs, concentrations of xSO_4, NO_3 and Cl are higher at the forested Hafren (Table 5.7, Figure 5.19). Differences in NO_3 time series are particularly striking, since concentrations at the Gwy consistently fall below detection limits during summer, whereas those at the Hafren remain continuously elevated (Figure 5.19d). These patterns conform to Stage 1 and Stage 2 N saturation respectively as defined by Stoddard (1994) (Section 5.1.2). Since there are no other major differences between sites, it is probable that the more advanced N saturation stage at the Hafren can be attributed to the effects of afforestation. As would be expected given the higher xSO_4 and NO_3 levels, the Hafren is more acidic, with lower pH and higher labile Al concentrations. However differences between streams, particularly for alkalinity, are less pronounced than in the Galloway or Trossachs lochs. Results for the two Plynlimon streams are consistent with those of a previous study including the Gwy and Hafren by Reynolds *et al.* (1986), which showed that Na, Cl, SO_4, NO_3, Al and H^+ output fluxes were enhanced by forestry.

5.5.4 Summary

The three sets of closely located forest and moorland catchments in the UKAWMN suggest a consistent pattern of water chemistry response to afforestation. In each case, the forested site exhibits higher concentrations of xSO_4, NO_3 and marine ions, lower pH and alkalinity, and higher labile Al. Afforestation has previously been cited as a cause of increased acidification in a range of studies (e.g. Nilsson *et al.*, 1982; Stoner and Gee, 1985; Jenkins *et al.*, 1990), with the main mechanisms thought to be enhanced dry and occult deposition to the forest canopy (Mayer & Ullrich, 1977); base cation uptake from the soil by the growing forest (Miller, 1981); and decreased water yield concentrating pollutants in surface waters (Neal *et al.*, 1986). The importance of uptake appears to be low at the UKAWMN sites, since non-marine base cation concentrations are generally at least as high at forested as at moorland catchments. However, forests in the UKAWMN catchments are generally at or close to maturity and it is probable that uptake was more important in the past. NO_3 uptake is also likely to have been higher in the past when biological requirements were greater (Emmett *et al.*, 1993).

Table 5.7

Mean values of major chemical determinands for paired forested and moorland catchments

SITE	Alkalinity	pH	xSO$_4$	NO$_3$	Cl	Ca	Mg	Na	Al$_{lab}$	Non-labile Al	DOC
Loch Chon (F)	4.8	5.6	49	12	223	78	51	191	20	40	3.2
Loch Tinker (M)	18.8	6.1	39	3	163	85	48	143	3	18	4.7
Loch Grannoch(F)	-13.9	4.6	72	17	257	48	54	223	225	81	4.3
Round Loch (M)	-6.1	4.9	47	7	195	33	46	174	60	35	3.0
Afon Hafren* (F)	5.5	5.4	62	21	205	44	65	188	105	80	2.0
Afon Gwy (M)	5.9	5.6	48	11	159	40	54	146	56	57	2.1

* Means for Afon Hafren based on April 1991 to March 1998 data, corresponding to shorter record at Afon Gwy. (F) = forested; (M) = moorland. All variables in µeq l^{-1} except pH, Al (µg l^{-1}) and DOC (mg l^{-1}).

Table 5.7 demonstrates that mean xSO$_4$ concentrations are 26%, 53% and 29% greater at Loch Chon, Loch Grannoch and the Afon Hafren respectively, than their moorland pairs. The equivalent increases in Cl are 37%, 32% and 29%, whilst NO$_3$ is increased by a factor of between two and four. The disproportionately large increases in NO$_3$ suggest that enhanced N inputs have increased the degree of N saturation in forested soils, and this is supported by seasonal NO$_3$ patterns at forested sites characteristic of more advanced saturation stages. It should be noted that since none of the three forested catchments has been planted over more than 70% of its area, an entirely forested catchment would be expected to show even larger increases in acid anion concentrations, and hence greater acidification.

■ 5.6 Summary

- Spatial variations in water chemistry appear generally consistent with deposition; concentrations of xSO$_4$ are lowest at relatively unimpacted northwestern sites, and highest in more polluted southern and eastern areas. NO$_3$ variations are similar, ranging from near-zero concentrations at low impacted sites to substantial leaching at some higher deposition sites, indicative of advanced stages of nitrogen saturation.

- Relationships between deposition and surface water chemistry are complicated by a range of catchment-specific factors. A comparison of paired moorland and forest catchments supports the conclusion that afforestation causes increased SO$_4$ and NO$_3$ concentrations in runoff, and hence greater acidity. Catchment altitude also appears to be an important influence on N leaching, whilst variation in geological buffering capacity further complicates spatial patterns in pH and alkalinity.

- Temporal trend analysis suggests limited chemical recovery at UKAWMN sites during the last decade. Decreases in xSO$_4$ were restricted to the River Etherow, Lochnagar and Old Lodge, all in central/eastern locations with relatively high dry deposition inputs. The lack of downward trends elsewhere may result from; (a) smaller S deposition reductions in areas dominated by wet deposition; (b) high short term variability masking relatively small expected decreases; (c) inter-annual xSO$_4$ fluctuations linked to climate, specifically variations in sea-salt inputs; and (d) possible

desorption of sulphur stored in catchment soils. Since the mid-1990s, xSO_4 appears to have declined at a larger number of sites, which may indicate the start of more widespread recovery.

- In accordance with the lack of widespread xSO_4 reductions, few sites exhibit clear recovery in pH and alkalinity. At the three sites with declining xSO_4, NO_3 has increased, and at the Etherow and Old Lodge base cations have decreased. In addition, organic acidity (i.e. DOC) has increased at all three sites. These changes appear so far to have offset any positive impact of xSO_4 reductions. At Lochnagar, NO_3 increases have been sufficient to cause continued loch acidification. At all sites, it appears that chemical recovery will require substantial further reductions in S and N deposition.

- Significant increases in pH and alkalinity were observed at six and four sites respectively, but in the absence of downward trends in acid anion concentrations it is not possible to confidently attribute these changes to deposition reductions at this stage.

- Increases in NO_3 at Lochnagar, Round Loch of Glenhead, Loch Chon and the River Etherow suggest increasing N saturation at these catchments. However, direct links between N deposition and runoff at many sites may be masked by natural episodicity, seasonality and climatically-driven inter-annual cyclicity. It is believed that spring NO_3 maxima in surface waters may be inversely related to winter temperature, with variations driven by the North Atlantic Oscillation.

- Major increases in DOC concentrations have been observed at many sites; significant rising trends have been identified at 19 of the 22 UKAWMN sites, with concentrations at six sites having doubled or more during the last decade. These trends are of particular importance to the UKAWMN, since increases in organic acidity could reduce or even negate any increases in pH or alkalinity resulting from reductions in mineral acidity. At present the cause of these increases cannot be identified with confidence, although one proposed mechanism is the increased microbial decomposition of soil organic matter due to increasing summer temperatures. This mechanism would, under a scenario of increasing global temperatures, be expected to lead to further increases in DOC and colour levels in upland waters. The biological impacts of these changes are likely to be varied, including reduced light penetration due to increased water colour, and reduced fish toxicity under acidic conditions due to organic complexation of aluminium.

- Inter-annual cyclicity in sea-salt deposition appears to be a major cause of chemical variation in the UKAWMN dataset. The majority of sites are close to western or southern coasts, and receive large sea-salt inputs during westerly or southwesterly frontal storms. The frequency of these storms has been shown to vary substantially from year to year, with maxima associated with high winter values of the North Atlantic Oscillation Index. Marine ion concentrations at near-coastal sites have therefore shown highly consistent cyclical variations, with a major peak during the high NAOI 1989-1991 period. Cation exchange processes (the 'sea-salt' effect) have led to associated cyclical variations in non-marine cations, including H^+ and labile Al, generating more acidic conditions in high sea-salt years. Periods with high NAO Index are also associated with high rainfall, and this will also increase acidity through cation dilution. It is suggested that a parallel process of marine SO_4 adsorption and desorption may operate, leading to cyclical fluctuations in calculated xSO_4 that are unrelated to variations in pollutant S deposition.

- Climatically-driven cyclicity in important chemical variables, such as xSO_4, NO_3, and pH, has important implications for trend detection. Cyclical variations may either mask underlying, anthropogenically-driven trends, or generate spurious trends. The approximately decadal timescales over which these variations appear to operate imply that monitoring will need to operate over long periods in order to adequately assess the impact of anthropogenic factors on surface water quality.