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# Trends and seasonality in stream water chemistry in two moorland catchments of the Upper River Wye, Plynlimon

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## Abstract

Stream water chemistry in the Cyff and Gwy subcatchments within the headwaters of the River Wye has been monitored regularly since 1980. In the Gwy, which is a predominantly semi-natural grassland catchment, land use has remained relatively static over the monitoring period, whilst the Cyff catchment is more buffered because of base cation inputs from agricultural improvement and ground water sources. Using a variety of statistical techniques, the long-term data are examined for evidence of trends after eliminating seasonal effects. The results highlight some of the difficulties associated with the analysis of long-term water quality data which show considerable variability over a variety of timescales. Some of this variability can be explained in terms of hydrochemical responses to climatic extremes and episodic events such as large atmospheric inputs of seasalts. The long-term fluctuations in solute concentration underline the continuing need for maintaining consistent long-term monitoring at sensitive upland sites if underlying trends related to gradual changes in pollutant deposition or climate are to be detected with any certainty.

## Introduction

Sensitive upland ecosystems have been increasingly subject to the effects of large scale environmental disturbances such as acid deposition since the onset of the industrial revolution in the nineteenth century (Renberg and Battarbee 1990). More recently, following extensive research over the last 25 years, various international protocols have been implemented to limit acid pollutant emissions in order, at the very least, to reduce current and future impacts and, hopefully, to promote ecosystem recovery (Wright and Hauhs 1991). Whilst relatively sophisticated hydrochemical models such as MAGIC (Cosby *et al.* 1985) and SAFE (Sverdrup *et al.* 1995) can be used to predict the historical impact of acid pollutants and the likely future trajectory for recovery, these models contain considerable uncertainties and their predictions are difficult to validate. As a consequence, long-term hydrochemical monitoring provides one of the few ways of evaluating the response of freshwater ecosystems to pollutant emission control strategies, although differentiating response trends from a background of 'natural' episodic,

seasonal and decadal changes remains a considerable challenge (Turk 1983; Aulenbach *et al.* 1996).

This paper presents the results of over 16 years of hydrochemical monitoring of two streams draining moorland catchments at Plynlimon. Over the monitoring period, land use has remained relatively unchanged within the catchments, thereby removing one major source of variability in the hydrochemical record. The data are explored using statistical trend analysis techniques and the results are discussed in relation to the processes likely to influence solute chemistry.

## Sites and Data

Hydrochemical data have been collected from the outlet of the Afon Cyff and the Afon Gwy subcatchments in the Upper Wye at Plynlimon since 1980. The catchments, which are described in detail in Reynolds *et al.* (1989) and Kirby *et al.* (1991), are topographically similar, each covering an area of c.3.5 km<sup>2</sup> with an altitude range between 350 and 700 m above sea level. The catchments are underlain by base-poor Lower Palaeozoic shales, mudstones and

grits covered by a mosaic of nutrient-poor acid upland soils. In their semi-natural state, the peaty-topped mineral soils support acid grassland vegetation communities whilst dwarf shrub communities dominate the hilltop peats. The latter are more extensive in the Gwy catchment, accounting for 37% of the area compared to 14% in the Cyff. Over the last 40 years thirty nine percent of the Cyff and 7% of the Gwy catchment have been improved agriculturally by the addition of lime, fertilisers and by reseeded with more productive grasses (Hornung *et al.* 1986). Over the 16 year monitoring period, however, the level and aerial extent of agricultural improvement has remained static, although some areas within the Cyff have received maintenance additions of lime and fertiliser.

Over the sixteen years, stream water sampling has been carried out at frequencies varying between weekly and monthly. In each catchment, samples were collected upstream of the flow gauging structures from which flow at time of sampling was recorded. The protocol for sample collection and pre-treatment has remained the same over the 16 year period. On return to the laboratory, pH was determined on an unfiltered subsample using a Radiometer pH meter and electrodes. The remaining sample was filtered through 0.45 µm membrane filters prior to analysis for major cations and anions. The analysis of base cations was performed at ITE Bangor. Calcium and Mg were measured by flame atomic absorption spectrophotometry following addition of lanthanum chloride. For the first 18 months of monitoring, Na and K were determined using a flame photometer. This method proved to be too insensitive for K at the low concentrations encountered in the streams, so subsequent analyses for both Na and K were performed by flame emission spectrophotometry using a Perkin-Elmer model 280 atomic absorption spectrophotometer (Reynolds *et al.* 1986; 1988). Up to September 1984, NO<sub>3</sub>-N and Cl were determined colorimetrically at ITE Merlewood using an autoanalyser whilst SO<sub>4</sub>-S was measured using an automated turbidimetric technique. Subsequently, all anion analyses were performed using a Dionex ion chromatograph. The different methods were run concurrently for 3 months and the results were cross checked extensively to ensure that the methodological changes did not bias the data.

Mean monthly air temperature and monthly rainfall data were obtained from the Moel Cynedd weather station for the sixteen year period. Flow data from the Cyff catchment only are presented as it was discovered, subsequent to analysis, that flow data from the Gwy had been affected by a calibration change to the flow gauging structure which had not been incorporated into the analysed data set. The close proximity of the two catchments means that flow patterns are extremely similar, although absolute amounts of runoff differ because of the different sizes of the catchments.

## Statistical Methods

Two techniques were used for trend analysis; the seasonal Kendall test (Hirsch *et al.* 1982) and a seasonal Box-Jenkins time series model (O'Donovan 1983). The seasonal Kendall test is a non-parametric test developed from the Kendall tau test for the detection of monotonic trends in time series data. Its development was aimed towards application to water quality time series data with the main objectives of overcoming the problems associated with applying equivalent parametric tests. Thus, the test is based on ranked data, and is robust against censored, missing or extreme values which are often encountered in water quality data. Furthermore, the test does not require adherence to a normal distribution; this is important since water quality data often show a strong relationship with flow, seasonality, serial dependence and a skewed distribution (usually positive). An extension to the seasonal Kendall test was developed to accommodate the problems of serial correlation in the data (Hirsch and Slack 1984), although this modified version is thought to be more powerful than the original test only for long term data sets (> 5 years) and where autocorrelation is less than 0.6.

The Seasonal Kendall test was applied to both data sets over the 16 year period. Because the sampling intervals varied, a set of calendar monthly averaged values was generated for the period January 1980 to December 1995. Data for DOC were absent from June 1981 to August 1984 due to instrument failure. For SO<sub>4</sub>-S, data for time series analysis were restricted to the period from January 1985 onwards as the chemical data from the turbidimetric method contained an unacceptable amount of scatter.

Seasonal Autoregressive Integrated Moving Average Box-Jenkins time series models (SARIMA; O'Donovan 1983) were also fitted to the monthly summarised data. Box-Jenkins methods provide a wide and flexible range of models which can incorporate seasonal, autoregressive (observations correlated with previous observations) and moving average (observations correlated with previous residuals) components. They have proven reliability in a number of disciplines. The residual series from the models is assumed to be independently normally distributed. With some chemical determinations, which occasionally produce extreme high values, log transformation of the observed data may be beneficial in achieving this assumption. For consistency, a model incorporating a seasonal (annual) difference, a seasonal first order moving average term and a first order autoregressive term, to account for serial dependence, (technically a  $(1,0,0) \times (0,1,1)_{12}$  model) was fitted to all calendar monthly data. The estimate of the differenced term and its standard error provide an estimate of the underlying per annum trend in the data.

Large and complex data sets of the type described here often confound interpretation. Their multivariate nature often masks relationships so that simple graphical techniques can prove extremely useful for visualising the data

and identifying trends and relationships. LOWESS (locally weighted scatterplot smoothing) has been used to simplify, graphically, the underlying pattern within the time series of determinations from individual catchment visits. Patterns of seasonal variation were visualised by plotting histograms of the 16-year monthly average concentrations for each solute.

## Results

The 16 year average concentration data in Table 1 are consistent with earlier studies of the catchments (Reynolds *et al.* 1986) showing the Cyff to be more base rich and better buffered than the Gwy with higher mean, minimum and maximum values for pH and for Ca and Mg concentrations. Sodium and Cl are derived almost exclusively from atmospheric deposition at Plynlimon (Neal *et al.* 1986), and consequently show very similar long-term values in each catchment as does silicon which is derived from weathering. Mean and maximum concentrations of SO<sub>4</sub>-S, DOC and K tend to be larger in the Cyff. In contrast, mean NO<sub>3</sub>-N concentrations are very similar in the two catchments, although the Cyff has a larger maximum value.

Despite differences in the absolute magnitude of the concentrations, the similarities in the long term and sea-

sonal patterns of variability for each solute in the two catchments are so strong that for the majority of solutes example plots are given for one catchment only. Sodium and Cl both fluctuate irregularly over the 16 years, with concentration peaks in 1984 and 1990–91 (Figure 1). Seasonal maxima in concentrations occur in February and March with lowest values observed in August (Figures 2 and 3). Visually, the suggestion of a trend of increasing Na concentrations over time is not apparent for Cl (Figure 1).

The long term variations in pH and in Ca, Mg and Si concentrations (Figure 4) at the two sites are also similar, although pH variation is rather less damped than for the three solutes. Peak values occur in 1984 and for pH and Ca there are subsequent peaks in 1989. Seasonally, patterns of variation are quite different (Figure 2 and 3). Calcium concentrations and pH have mid-summer maxima and winter minima which are the reverse of the pattern for Si. The seasonal variation in Mg concentrations shows a similar but slightly more damped pattern to Ca (Figure 2). There is little visual evidence from the LOWESS plots of a trend in concentration over the 16 years except for pH in the Gwy which appeared to have increased from 1979 to 1990 (Figure 4).

Nitrate-N concentrations show strong oscillations over the 16 years with peaks in 1985 and 1992 (Figure 5). Nitrate-N is highly seasonal with summer minima and winter maxima (Figure 3). In contrast, K which has a similar seasonal pattern (Figure 2), shows less long-term variability although concentrations may be increasing from 1988 onwards (Figure 5). The plots also reveal the relatively poor sensitivity of the analytical method for K employed in the first 18 months of the study. Sulphate-S shows very little long-term variability although there is an indication of a steady decline in the Gwy catchment but not in the Cyff (Figure 6). There is relatively little seasonal variation in SO<sub>4</sub>-S, although there is a suggestion of a summer maximum in the Cyff and summer plus autumn/winter maxima in the Gwy (Figure 3).

The LOWESS plots for DOC suggest that concentrations are increasing although there is considerable variability over time (Figure 6). Unfortunately, instrumental problems resulted in the loss of a considerable amount of data during the early 1980s. Seasonally, DOC concentrations increase steadily from May through to August and then decline to an April minimum (Figure 3).

The statistical analyses of trends yield both comparable and contrasting results between catchments and solutes. Overall, the seasonal Kendall test indicates a greater number of significant trends compared to the SARIMA models, although levels of significance are relatively small for some solutes eg Mg in the Gwy ( $p < 0.05$ ) and Cl in the Cyff ( $p < 0.05$ ) (Tables 2 and 3). In addition, the LOWESS plots are not always consistent with the test and model results, although for some solutes there is good agreement amongst all three approaches (eg pH in the Gwy). The most comparable results between the seasonal Kendall test

Table 1. Summary of streamwater chemistry over 16 years in the Cyff and Gwy catchments at Plynlimon. All concentrations in mg l<sup>-1</sup> except pH.

Cyff	Mean	Min	Max
Ca	1.87	0.40	4.08
Mg	0.99	0.49	1.76
Na	3.50	2.10	5.60
K	0.12	<0.01	0.66
Cl	5.81	3.10	12.0
SO <sub>4</sub> -S	1.73	0.34	4.60
NO <sub>3</sub> -N	0.14	<0.01	0.93
DOC	2.00	0.20	13.3
pH	6.22	4.74	7.26
Si	1.12	0.35	2.00
Gwy	Mean	Min	Max
Ca	0.86	0.34	1.56
Mg	0.69	0.22	1.14
Na	3.32	1.80	5.40
K	0.09	<0.01	0.50
Cl	5.59	2.90	12.0
SO <sub>4</sub> -S	1.22	0.05	3.30
NO <sub>3</sub> -N	0.15	<0.01	0.67
DOC	1.81	<0.05	8.00
pH	5.49	4.21	6.90
Si	1.09	0.32	1.90

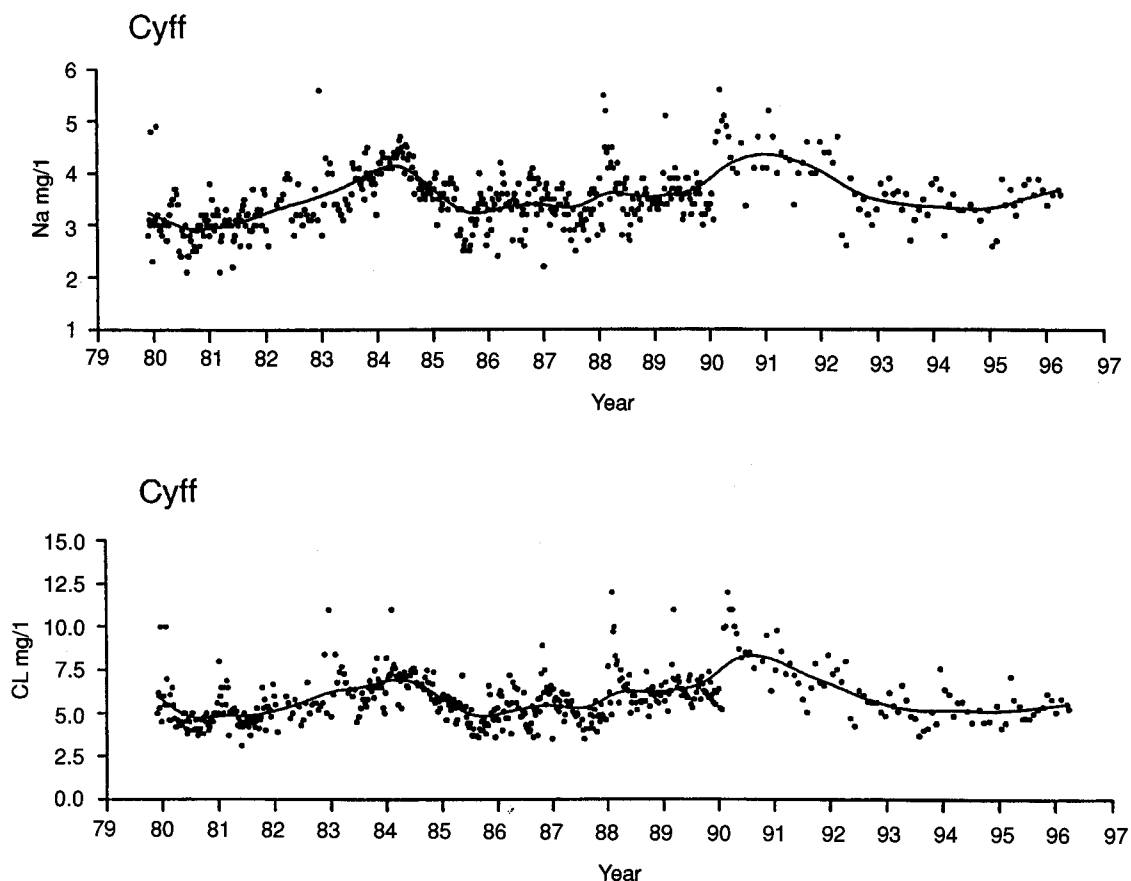


Fig. 1. Time series plots for Na and Cl concentrations in the Cyff showing LOWESS trend lines.

and the SARIMA models are for K and  $\text{SO}_4\text{-S}$  in the Gwy (Tables 2 and 3). Both show significant trends ( $\text{SO}_4\text{-S}$  decreasing and K increasing), with similar per annum changes (c.  $-0.015 \text{ mg SO}_4\text{-S l}^{-1} \text{ a}^{-1}$  and  $+0.002 \text{ mg K l}^{-1} \text{ a}^{-1}$ ); the test and model results are also consistent with the LOWESS plots. All three approaches show an increasing, significant trend in pH in the Gwy, although the per annum pH change for the seasonal Kendall test ( $+0.025 \text{ pH units a}^{-1}$ ) is just under twice that predicted by the SARIMA model.

The seasonal Kendall test indicates a significant upward trend for Na in both streams which is consistent with the LOWESS plots. The per annum increases ( $0.03$  and  $0.04 \text{ mg l}^{-1} \text{ a}^{-1}$ ) are very similar to those in the SARIMA model which yields results which do not quite achieve significance. For DOC, the seasonal Kendall test results are again consistent with the LOWESS trends. The SARIMA model for DOC in the Gwy also predicts a significantly increasing trend but with a per annum change ( $0.05 \text{ mg l}^{-1} \text{ a}^{-1}$ ) of about half that of the seasonal Kendall test. The

SARIMA model for DOC in the Cyff does not achieve significance.

## Discussion

The variation in consistency amongst the three methods of assessing trends exemplifies some of the difficulties of identifying, with certainty, trends in water quality data. These uncertainties have been discussed extensively by Robson and Neal (1996), who point out some of the pitfalls in a purely statistical approach when this is detached from a visual assessment using graphical techniques. A number of caveats must be considered when interpreting trend analyses. For example, the seasonal Kendall test does not allow for cyclic patterns in the data as it assumes an underlying monotonic trend, yet the LOWESS smoothing plots indicate strong cyclical patterns for several solutes. Trends in any particular ion must also be balanced by approximately equal trends in counter ions and must be greater than the uncertainty in the chemical analysis. For

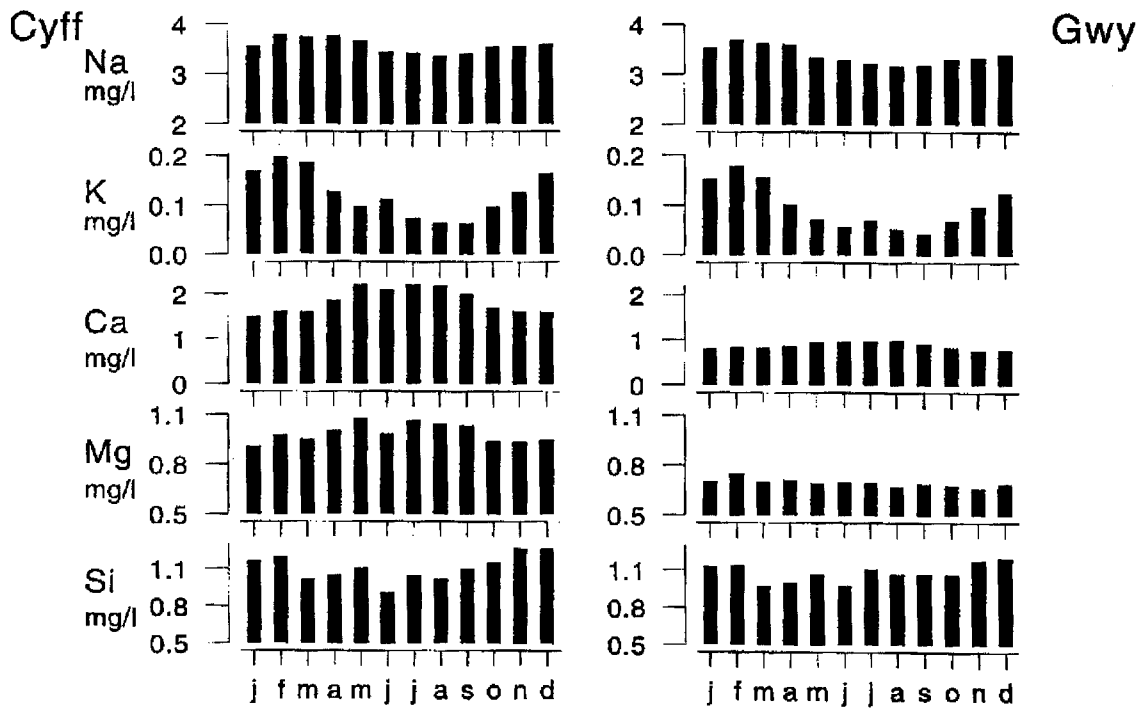


Fig. 2. Bar charts showing variations in monthly mean concentrations of base cations and Si.

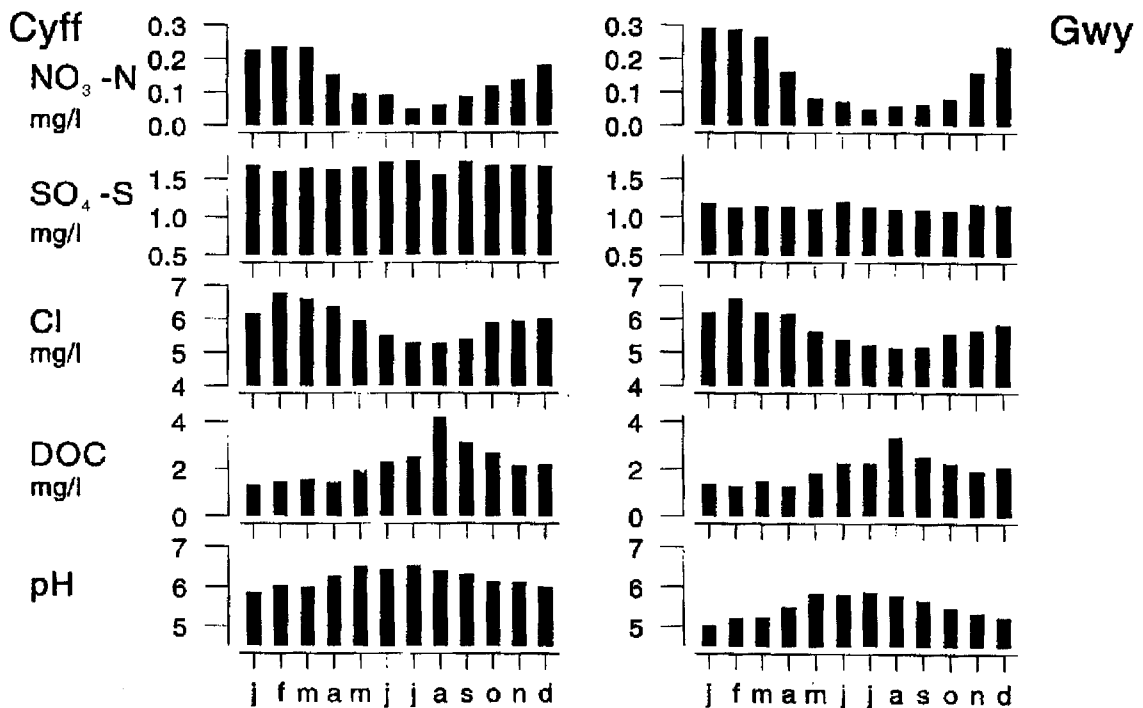


Fig. 3. Bar charts showing variations in monthly mean concentrations of anions, DOC and pH.

Table 2. Results of the seasonal Kendall test for the Cyff and the Gwy. For each site and solute the first figure is the per annum change and the figure in brackets is the significance of the change.

	Cyff		Gwy	
Na mg l <sup>-1</sup>	0.030	(0.0005)	0.040	(0.0001)
K mg l <sup>-1</sup>	0.000	(NS)	0.002	(0.005)
Ca mg l <sup>-1</sup>	-0.003	(NS)	0.009	(0.005)
Mg mg l <sup>-1</sup>	0.000	(NS)	0.004	(0.05)
Si mg l <sup>-1</sup>	0.002	(NS)	0.010	(0.01)
NO <sub>3</sub> -N mg l <sup>-1</sup>	0.014	(NS)	0.000	(NS)
SO <sub>4</sub> -S mg l <sup>-1</sup>	-0.011	(NS)	-0.014	(0.0005)
Cl mg l <sup>-1</sup>	0.040	(0.05)	0.070	(0.0001)
DOC mg l <sup>-1</sup>	0.110	(0.0001)	0.100	(0.0001)
pH	0.014	(0.05)	0.025	(0.0005)
Flow l s <sup>-1</sup>		-3.000 (0.05)		
Temperature °C		0.040 (NS)		
Rainfall mm		0.010 (NS)		

those solutes for which there is agreement across all three methods, the total change over the 16 years predicted by the models is greater than the analytical uncertainty. However, for most solutes with significant trends, the size of the per annum trend is small relative to the amount of scatter in the time series, underlining the need for both visual interpretation and long-term data with a high sampling frequency. More elaborate models incorporating climatic and other environmental variables as covariates may improve the ability to detect trends.

Nitrate-N concentrations show strong seasonality (Figure 3) reflecting the seasonal change in the availability

of N for leaching within the catchment. This regular seasonal pattern was disrupted following the dry summers of 1984 (Reynolds *et al.* 1992), 1990 and 1995 (Figure 5). Indeed, the data indicate that the downward trend in NO<sub>3</sub>-N from the beginning of the record may relate to the severe drought in 1976 although there is considerable uncertainty attached to LOWESS trend lines at the beginning and end of a time series. The long-term fluctuations in stream water NO<sub>3</sub>-N concentrations appear, therefore, to be related to climatic extremes making it very difficult to discern trends relating to changes in atmospheric N deposition. This is not surprising given the large size of

Table 3. Results of applying SARIMA time series models to the Cyff and Gwy data. For each site and solute the first figure is the estimated per annum change and the figure in brackets is its standard error. Estimates exceeding twice their standard error are indicated by an asterisk.

	Cyff		Gwy	
Na mg l <sup>-1</sup>	0.027	(0.016)	0.028	(0.019)
K mg l <sup>-1</sup>	0.001	(0.001)	0.002	(0.001)*
Ca mg l <sup>-1</sup>	-0.002	(0.011)	0.004	(0.005)
Mg mg l <sup>-1</sup>	-0.001	(0.004)	0.000	(0.003)
Si mg l <sup>-1</sup>	0.000	(0.005)	0.002	(0.005)
NO <sub>3</sub> -N mg l <sup>-1</sup>	0.001	(0.003)	-0.001	(0.003)
SO <sub>4</sub> -S mg l <sup>-1</sup>	-0.001	(0.014)	-0.017	(0.008)*
Cl mg l <sup>-1</sup>	0.034	(0.046)	0.038	(0.045)
DOC mg l <sup>-1</sup>	0.049	(0.035)	0.046	(0.024)*
pH	0.011	(0.007)	0.014	(0.008)*
Flow l s <sup>-1</sup>		0.770 (3.770)		
Temperature °C		0.047 (0.025)		
Rainfall mm		0.32 (1.67)		

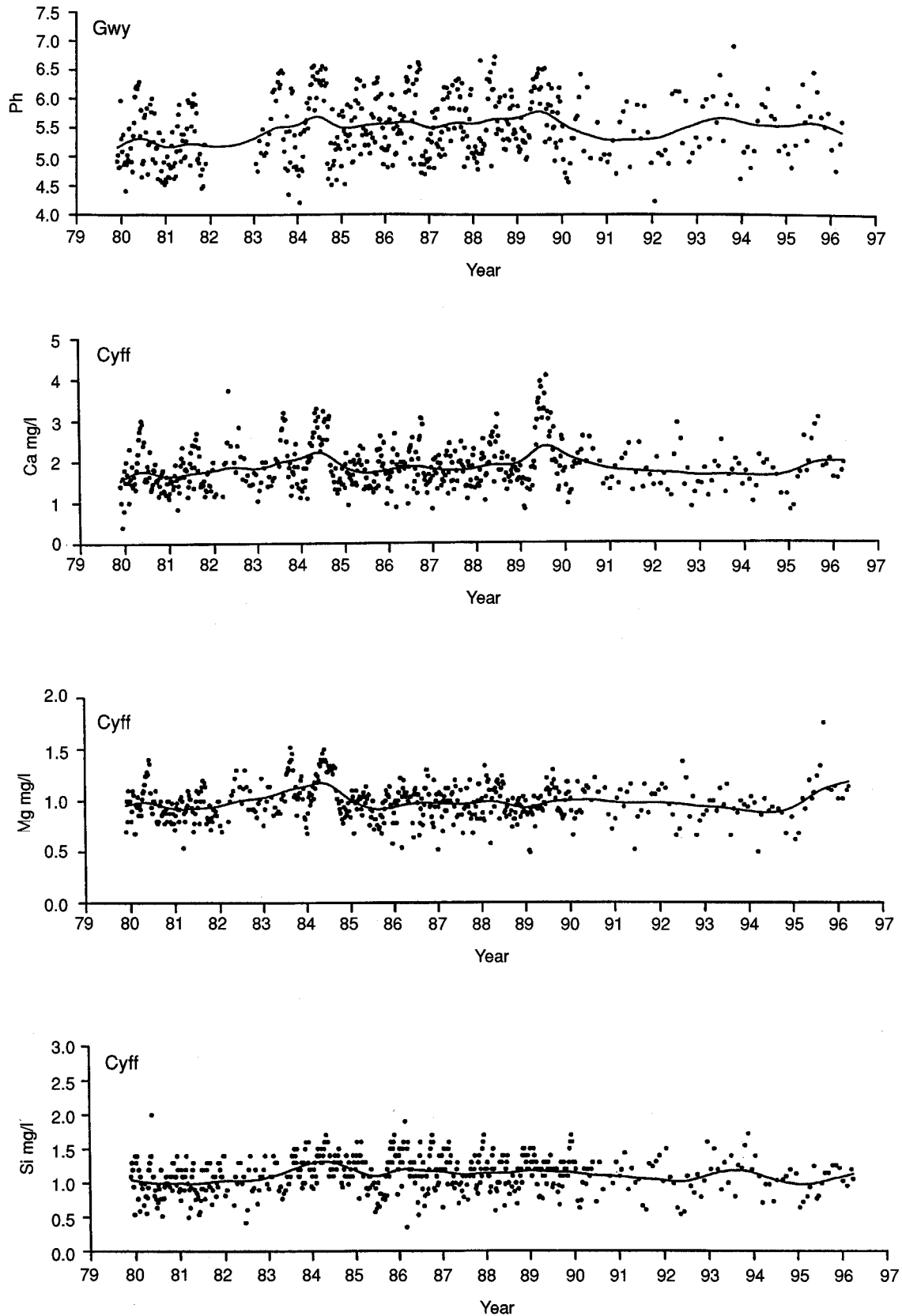


Fig. 4. Time series plots for pH in the Gwy and for Ca, Mg and Si concentrations in the Cyff showing LOWESS trend lines.



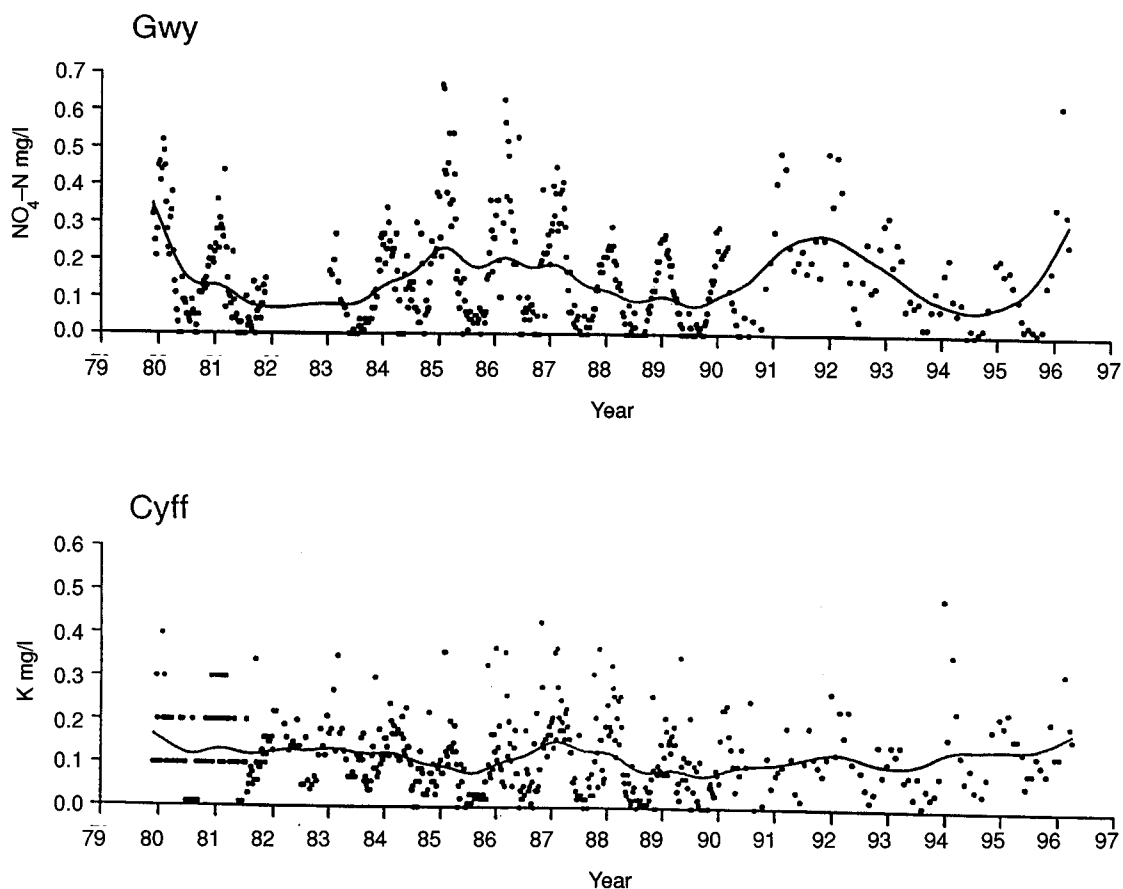


Fig. 5. Time series plots for  $\text{NO}_3\text{-N}$  in the Gwy and for K concentrations in the Cyff showing LOWESS trend lines.

the soil-plant N pool in upland systems and the major influence of biological processes over the fate and behaviour of atmospherically deposited N (Batey 1982). Furthermore, where such strong patterns are evident, the length of record available for time series analysis becomes crucial to the interpretation of the result (Robson and Neal 1996). An earlier analysis of the same two data sets for the period between October 1984 and September 1995 revealed a small but significant downward trend in  $\text{NO}_3\text{-N}$  concentrations. This result was an artefact of the choice of time interval which commenced at a peak and finished in a trough.

Concentrations of DOC in streams are strongly mediated by biological processes as reflected by a steady build up in concentration through the spring to an August maximum in both streams. The significant upward trend in DOC observed in the Cyff and Gwy is consistent with the results of other studies (McDonald *et al.* 1989; Kay *et al.* 1989; Neal and Robson 1996) which have reported increases either in DOC or water colour (which is related to DOC). It is unclear why DOC concentrations should be increasing although re-wetting following drought can

result in large episodic concentrations which may bias the trends. The widespread nature of the result suggests a global influence on the processes regulating DOC generation/retention in organic-rich soils which may be climatic or linked to the changing deposition of acidity and nitrogen in upland areas.

At Plynlimon, large, periodic increases in stream water Cl concentrations are associated with major deposition episodes and it may take several months or even years for the Cl pulse to move through the catchment (Neal *et al.* 1988). In addition, drought can increase the residence time of Cl in the catchment leading to a Cl build up in soil solution which may take months to deplete (Reynolds and Pomeroy 1988). Singly or in combination, these processes can account for the long-term fluctuations in both Cl and Na. For example in February 1988, a large seasalt deposition event yielded a fortnightly rainfall concentration of  $16 \text{ mg l}^{-1}$  Na and  $29 \text{ mg l}^{-1}$  Cl (approximately 8 times the annual average value) resulting in an immediate response in the streams (Figure 1). It took nearly 6 months for the Cl pulse to decay. Following two large deposition events in February and March 1990 (with concentrations in fort-

nightly precipitation samples of  $11 \text{ mg l}^{-1} \text{ Na}$  and  $21 \text{ mg l}^{-1} \text{ Cl}$ ), the dry summer of that year appears to have prolonged the residence time of the deposited salt, leading to an extended decay period over the next two years (Fig. 1). Such extreme events are difficult to incorporate into traditional seasonal time series models.

There is now considerable interest as to whether declining sulphur dioxide emissions (Gilham *et al.*, 1992) are reflected in declining levels of acidity and sulphate in rain-

fall and acid sensitive streams. Although analysis of trends in wet deposition data from Plynlimon since 1983 provide no strong evidence of an increase in pH or of a decline in non-seasalt sulphate inputs (Robson and Neal 1996; Vincent *et al.*, 1996), all three trend analysis techniques indicate an increase in stream water pH and a decrease in  $\text{SO}_4\text{-S}$  concentrations in the Gwy over the last 16 years. The pH and buffering characteristics of this stream imply that it is likely to be sensitive to changes in acidifying

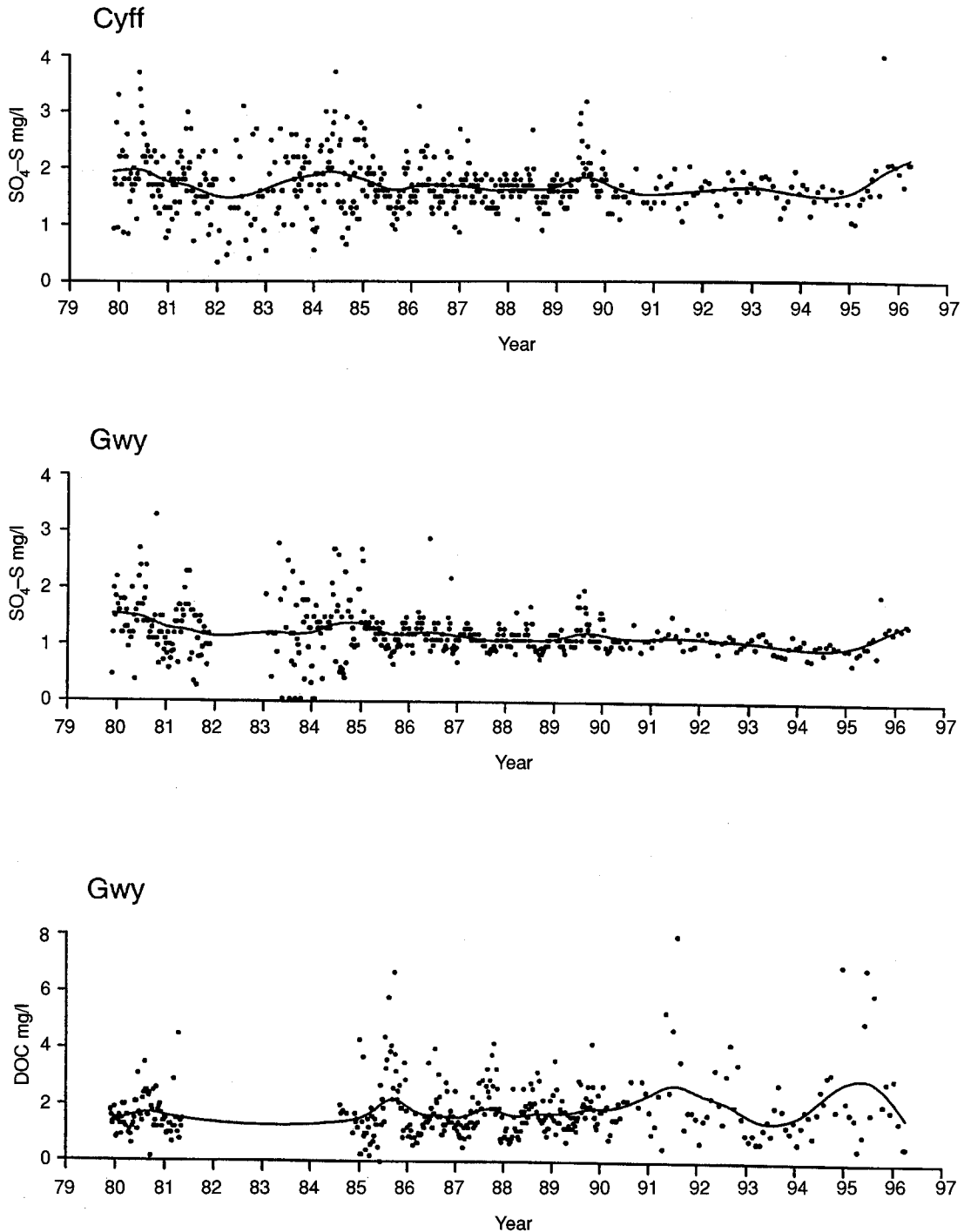


Fig. 6. Time series plots for  $\text{SO}_4\text{-S}$  concentrations in the Cyff and for  $\text{SO}_4\text{-S}$  and DOC in the Gwy showing LOWESS trend lines.

inputs in contrast to the better buffered Cyff where no significant pH change has been recorded. As noted earlier, land use in the Gwy has remained relatively static over the observation period, particularly with respect to afforestation and agricultural liming which would both confound any trend resulting from changes in acid deposition. Interestingly there is no significant  $\text{SO}_4\text{-S}$  trend in the Cyff. Average  $\text{SO}_4\text{-S}$  concentrations in the Cyff are greater than in the Gwy (Table 1) and the seasonal patterns also differ with a more pronounced summer maximum in the Cyff (Figure 3). This implies a low flow source of  $\text{SO}_4\text{-S}$  in the Cyff possibly related to ground water inflow and a source of sulphate from the oxidation of pyrite within the shale bedrock. Agricultural fertilisers (notably rock phosphate) also contain sulphur and more intense cultivation in the Cyff may have increased organic sulphur mineralisation rates (Hornung *et al.* 1986). Thus, there are several sulphur sources and release mechanisms which would mask any response to changes in atmospheric inputs to the Cyff catchment.

## Conclusions

Long-term monitoring at two moorland catchments at Plynlimon has revealed considerable variability in stream solute concentrations over a variety of timescales. Some of this variability can be explained in terms of hydrochemical responses to climatic extremes and episodic events such as large atmospheric inputs of seasalts. Long-term fluctuations in solute concentration underline the continuing need for maintaining consistent long-term monitoring at sensitive upland sites if trends related to changes in pollutant deposition or climate are to be detected with any certainty. Such monitoring sites should be carefully selected so that confounding influences of land use change or geological complexity do not obscure anticipated ecosystem responses. The statistical analysis of trends, which should always be accompanied by visual data inspection, is greatly empowered by monitoring protocols which maintain a consistent, frequent sampling routine. This requires a long-term funding commitment. The work described here has suffered the consequences of inconsistent financial support over the last 16 years and this has compromised the quality of the data collection. Despite these various obstacles, all three data analysis techniques (LOWESS smoothing, Seasonal Kendall test and Box-Jenkins SARIMA models) point to there being a steady decline in stream water  $\text{SO}_4\text{-S}$  concentrations and acidity in the acid sensitive Gwy catchment.

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