Scale dependence of the episodic hydrochemical response of nested catchments at Plynlimon

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Abstract

Previous monitoring of the surface water chemistry of the forested catchments at Plynlimon has concentrated on weekly measurements. Hence, peak values and details of the rapid changes in chemistry occurring during events tend to be missed, particularly for smaller catchments. Knowledge of the detailed hydrochemical response is necessary to predict effects on stream ecology and to quantify processes occurring within the catchment. This information is vital if the likely impacts of changes in landuse and pollutant input on episodic hydrochemical variations are to be modelled.

A summary of daily and three-hourly chemistry for the River Severn headwaters at Plynlimon, central Wales is presented. Data are from the summer and autumn of 1995 and the winter and summer of 1996. The effects of antecedent conditions, soil-type, landuse and groundwater and tributary inflow on stream episodic hydrochemical response are discussed for a range of spatial scales, including first, second and third order streams. Detailed information on the chemical changes due to a discrete groundwater inflow into the bed of one stream shows that, during episodes, its influence on stream chemistry is overridden by that of event water. A comparison of drainage ditch chemistry with main stream chemistry during storm events is used to consider the importance of tributary inflow at these times. The contrast in results between sites is assessed, to evaluate the effects of clearfelling and soil type on stream event chemistry.

Introduction

Rainfall events in acid-sensitive upland areas often promote rapid chemical changes in stream-water chemistry (UKAWRG, 1988). The most notable changes are a rapid decrease in pH, alkalinity and base cation concentrations and an increase in aluminium, in particular inorganic aluminium (Al^{3+}), as flow increases. As such catchments tend to have a 'flashy' runoff regime, large changes in flow and associated chemistry may occur in a matter of hours or minutes during storm events. The stress so caused to the stream ecosystem may result in the death of fish and other biological organisms (Ormerod and Jenkins, 1994), especially if the naturally acidic response of the stream has been enhanced by land-use change and increases in acid atmospheric pollutants (Harriman *et al.*, 1994). Although catchment processes contributing to acidification are still not fully understood, it is clear that changing flowpaths through hydrological events are of overwhelming importance in controlling the chemical character of episodes (Davies *et al.* 1992, Muscutt *et al.*, 1993, Wheater *et al.*, 1990, 1993).

During periods of low flow, a stream is fed mainly by water from the lower soil horizons and deeper groundwater. This typically has a high Acid Neutralisation Capacity (ANC) and low acidity, due to the weathering of base cations in the lower soil horizons and bedrock. However, during a rainfall or snowmelt event, most flow is derived from the upper, more acidic and aluminium-bearing soil horizons, causing the stream-flow chemistry to change, often dramatically. Hence, stream-flow may be thought of as consisting of two or more 'end-members' with different chemistries, the proportions of which change as discharge changes (Beck *et al.*, 1990, Wheater *et al.*, 1990, Christophersen *et al.*, 1990, Robson and Neal, 1990). To predict overall stream chemical response, therefore, requires understanding of the low flow chemistry, which reflects spatially varying controls on weathering processes, and the episodic response.

An important aspect of upland land-use management is afforestation, which may result in soil and stream acidification (Hughes *et al.*, 1990, Ormerod *et al.*, 1989, Reynolds *et al.*, 1988). Felling trees on such catchments may cause further medium-term (four to eight years) acidification of soils and streams due to increased nitrate leaching associated with a reduction in nitrogen uptake and

increased rates of mineralisation and nitrification (Neal et al., 1992a,b, Reynolds et al., 1995).

The long-term experimental catchments at Plynlimon were established initially to identify the hydrological effects of afforestation and to provide a suitable platform to observe the hydrochemical changes, in conjunction with effects of geology and soils. Stream chemistry has been monitored at Plynlimon for over a decade. This has been supplemented by detailed studies of rainstorm event response in a small catchment on the predominantly moorland area drained by the headwaters of the river Wye (Muscutt et al., 1993, Chapman et al., 1993, Hutchins et al., 1995). Previous studies of storm event response of the forested catchments focused primarily on pH and conductivity changes during events, which were related to flow, evaporation, dry deposition and the rainfall chemistry of prior events (Robson et al., 1992, 1993). Weekly sampling has taken place on the third-order Afon Hafren since 1983 and the second-order Nant Tanllwyth since 1991. In 1994, the fortnightly sampling of four first-order drainage ditches in the two catchments also began, to study the effects of forestry practices on stream-water chemistry. The weekly samples provide a general picture of chemical behaviour with increasing flows, but do not show the main chemical effects of a storm event due to the rapid stream responses.

This study addresses the episodic response of the forested catchments of the Upper Severn at Plynlimon and its spatial variability by:

(a) Analysis of the episodic stream chemistry data, collected at daily or three-hourly sampling intervals from seven stream-water sampling sites and five soil-water sampling sites, to enable a more detailed evaluation of the short-term variations in stream chemistry than was possible with weekly data;

(b) Discussion of the effects of scale, in particular with reference to the implications for hydrological flow pathways within the catchments. Chemical analysis of soil water, drainage ditch water and main stream water was required for this and careful selection of the sites also enabled the effects of felling and soil type to be considered within this nested sampling framework;

(c) Evaluation of episodic chemical data from both above and below a discrete groundwater inflow point in the Tanllwyth, to understand how this water pathway affects the episodic chemical response.

Experimental Site

Sampling was undertaken on the River Severn headwaters, located in the Hafren Forest at Plynlimon, central Wales. These cover an area of 1925 ha and have been the focus of extensive hydrological research since 1968 (Kirby et al. 1991). The area lies 24km inland from the Irish Sea and covers an altitude range of 320 to 740m. The Severn catch-

ments consist of two third-order streams, the Afon Hafren and Afon Hore, and the second-order Nant Tanllwyth, and their tributaries (Fig. 1). The mean annual rainfall, mainly frontal, from the west and south-west, accentuated by orographic effects is approximately 2500mm. It tends to be enriched in marine salts (Na, Mg, Cl and SO_4) while that from other trajectories may contain pollutant components (NH_4, NO_3, SO_4) of industrial or agricultural origin (Neal et al., 1994). The seasonal rainfall pattern has a maximum in autumn and winter and a minimum in May and June (Newson, 1979). Evaporation ranges from 400 to 650mm per year depending on the extent of forest cover, and the mean monthly air temperatures for February and August are 1.8°C and 13.1°C respectively (Reynolds et al., 1986). The site is underlain by undivided mudstones, shales and grits, of upper Ordovician and Silurian age. Some fault lines occur with associated calcite mineralisation.

The soils are typical of acid upland soils, consisting of peats, stagnopodzols, acid brown earths and stagnogleys. Drift deposits are locally derived, comprising stony boulder clay, shale or grit colluvium and valley bottom alluvium. The upper part of the Hafren catchment is covered by blanket peats and the lower part by stagnopozdols and some valley bottom peats, with a smaller central section of the catchment draining gleys. Valley bottom alluvium is found along the length of both the Hafren and Tanllwyth. Most of the Tanllwyth catchment drains stagnopodzols, although some tributaries flow over gleys. The very uppermost part of the catchment drains peats.
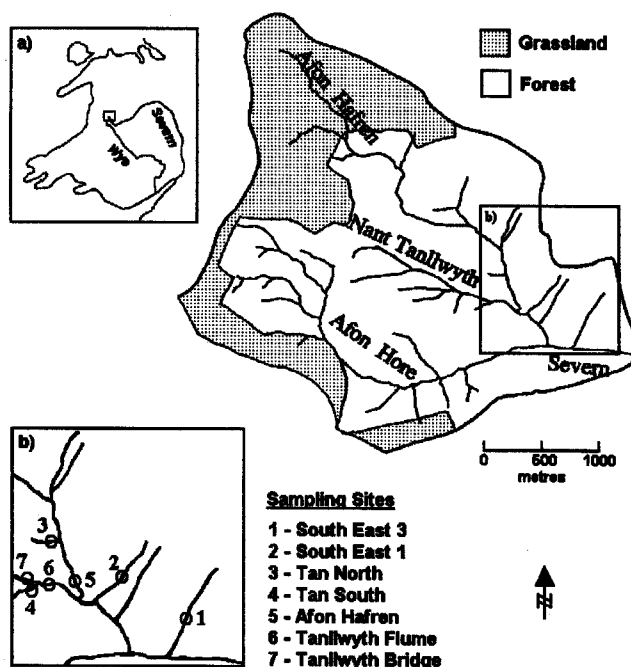

Fig. 1. *The River Severn headwaters at Plynlimon, Wales and their associated land-uses. Insert (a) shows their location within Wales and insert (b) shows the seven streamwater chemistry sampling sites.*

Although the upper part of the Severn catchment is covered by semi-natural acidic moorland peats, the predominant landuse is plantation forestry. Sitka Spruce (*Picea sitchensis*) and Norway Spruce (*Picea abies*) were planted in three phases between 1937 and 1974 (Fig. 1). Felling began in the Hafren catchment in 1995. Prior to planting, much of the area was ploughed and drainage ditches dug. This has altered the soil hydrology, allowing direct and rapid transport of soil-derived water to the main stream channels during storm events. This acid water, derived from near surface soil horizons, may therefore flow directly into the streams, increasing the acidity, aluminium and DOC concentrations at high flows (Reynolds and Hughes, 1989). The precise chemistry depends on the soil-type and the hydrological pathways from the soil to the stream.

Low flow stream chemistry shows significant spatial variability (Locks, 1996), reflecting heterogeneous groundwater inputs, and a number of shallow and deep boreholes have recently been drilled in the catchment to monitor groundwater chemistry (Neal *et al.*, 1997a,b). A 45m borehole was drilled in May 1994, approximately 5m from the Tanllwyth and 20m upstream of the flume where flow and chemistry are monitored. This was subsequently air flushed, which opened some fractures and enabled groundwater seepage into the stream. A rise in pH, conductivity and base cation concentrations during low flow periods was observed subsequently in the stream. In addition, water level measurements showed a positive head difference in the borehole relative to the stream; artesian conditions were observed during winter rainfall. The observed extent of water quality changes varied with flow, that for pH being most marked under intermediate flow conditions, with values increasing from 5.0 to about 6.3. No data were available for detailed episodic analysis at that time, so the impact of the groundwater inflow on chemistry during a storm event could not be assessed. It was noted, however, that the differences between stream chemistries measured above and below the inflow point were small during high flows.

Sampling Design and Methods

In this study in the Hafren forest, water samples were collected from six streams. The Afon Hafren, the Nant Tanllwyth both above (Tanllwyth Bridge) and below (Tanllwyth Flume) the discrete groundwater inflow point, and four small drainage ditches (Fig. 1(b)). The Afon Hafren catchment has an area of approximately 1300ha and the Nant Tanllwyth, 330ha (Locks, 1996). Streams of different order were selected so that the effects of scale on stream chemistry could be considered. The drainage ditches were also to be compared with soil water, to test the hypothesis that the former were representative of a spatially integrated measure of soil water chemistry.

Two ditches on each of two soils were selected for sampling. South-east 3 and South-east 1 drained podzolic soils, whereas Tan North and Tan South drained gleys. The soil type affected the flow regime of these ditches; Tan North and Tan South were ephemeral, as groundwater was apparently prevented from entering the stream by an impermeable clay layer, whereas SE1 and SE3 were perennial. Each of the pairs on each soil type consisted of one forested (Tan North and SE3) and one clearfelled site (Tan South and SE1), so that comparisons could be made between land-use. SE1 had been felled during 1995; felling of Tan South had been completed only weeks before the July 1996 sampling began.

Three programmes of sampling were undertaken (Table 1). Between 19 June 1995 and 30 September 1995, the two main streams (Tanllwyth Flume and Afon Hafren) and four first order streams (Tan N, Tan S, SE1 and SE3) were monitored daily, although the two ephemeral streams

Table 1. Periods of continuous monitoring and additional sampling undertaken during each of the three sampling Programmes.

Programme no.	Sampling Interval	Site(s)	Periods of Continuous Sampling	Other Samples taken during the day	Total no. of samples per site
1	Daily	Tan N, Tan S, SE1, SE3, Hafren & Tan Flume	13/7/95—9/8/95, 28/8/95—10/9/95 & 20/9/95—30/9/95	–	53
2	Daily	Tan Flume & Tan Bridge	8/1/96—11/2/96 (except 9/2/96)	–	34
3	3-hrly	Tan Flume	2/7/96—5/7/96 (except overnight 2–3 July)	8/7/96 (1 sample)	21
3	3-hrly	Tan Bridge	2/7/96—5/7/96 (except overnight 3–4 July)	8/7/96 (1 sample)	20
3	sub-daily to daily	SE1 & SE3	—	2–5 & 8 July '96 (1–4 samples)	10
3	sub-daily to daily	Tan N & Tan S	—	2–5 & 8 July '96 (1–2 samples)	5

Table 2. Summary of the daily chemistry of the six streams for Programme 1 (three periods during June to September 1995).

Solute	SE3 (FP)			SE1 (GP)			Tan N (FG)			Tan S (HG)			Hafren			Tanllwyth Flume		
	MAX	MIN	RANGE	MAX	MIN	RANGE	MAX	MIN	RANGE	MAX	MIN	RANGE	MAX	MIN	RANGE	MAX	MIN	RANGE
pH	6.83	5.32	1.51	6.65	5.78	0.87	4.82	3.86	0.96	4.99	3.95	1.04	7.17	4.52	2.65	7.36	4.18	3.18
Cond(μS/cm)	73.4	53.1	20.3	74.8	60.1	14.7	116.7	68.7	48.0	94.9	72.0	22.9	51.8	35.8	16.0	131.8	49.4	82.4
Ca (mg/l)	5.14	1.36	3.78	4.16	2.29	1.87	3.03	0.29	2.74	3.04	0.09	2.95	2.50	0.35	2.16	13.26	0.59	12.68
Mg (mg/l)	2.49	0.80	1.69	2.30	1.43	0.87	2.54	0.52	2.02	2.31	0.45	1.86	1.52	0.82	0.71	5.25	0.94	4.31
Na (mg/l)	5.41	3.81	1.60	7.30	5.23	2.07	6.71	4.38	2.33	6.67	4.75	1.92	5.20	3.77	1.43	7.19	1.62	5.57
K (mg/l)	1.176	0.038	1.138	0.57	0.031	0.539	0.826	0.025	0.801	1.373	0.029	1.344	0.803	0.028	0.775	0.702	0.093	0.609
SO$_4$ (mg/l)	16.31	8.25	8.06	11.20	7.53	3.67	13.77	6.43	7.34	11.99	6.09	5.90	5.94	3.03	2.91	8.71	5.11	3.60
Cl (mg/l)	8.70	5.59	3.11	11.72	9.86	1.86	9.46	5.00	4.46	9.68	7.37	2.31	7.71	5.03	2.68	8.61	6.41	2.21
Br (mg/l)	0.038	0.009	0.029	0.046	0.02	0.026	0.022	0.004	0.018	0.03	0.003	0.027	0.03	0.008	0.022	0.055	0.006	0.049
NO$_3$ (mg/l)	0.56	0.118	0.442	0.611	0.177	0.434	0.098	0.003	0.095	0.844	0.019	0.825	0.757	0.06	0.697	1.333	0.158	1.175
PO$_4$ (mg/l)	0.051	0.001	0.05	0.033	0.001	0.032	0.057	0.001	0.056	0.021	0.001	0.02	0.066	0.001	0.065	0.049	0.001	0.048
Al (mg/l)	0.205	0.001	0.204	0.163	0.002	0.161	0.493	0.156	0.337	0.562	0.345	0.217	0.398	0.003	0.396	0.564	0.001	0.563
NH$_4$ (mg/l)	0.347	0.013	0.334	0.325	0.013	0.312	0.162	0.0158	0.1462	0.125	0.016	0.109	0.456	0.012	0.444	0.224	0.012	0.212

could be sampled only when there was flow. Three storm events occurred during this period, on 14–19 July 1995, 3–5 September 1995 and 23–30 September 1995 (Alexander, 1997). A full analysis of all these daily samples taken prior to, during, and immediately after these events was undertaken to include pH, conductivity and all major cations and anions (Table 2). Flow from the two major streams was recorded every 15 minutes using Campbell data loggers at flumes that were located just downstream of the chemical sampling sites.

A second programme of daily sampling from 8 January 1996 to 11 February 1996 ascertained the influence of the groundwater inflow to the Tanllwyth from the borehole, by sampling above and below the inflow point. The upstream samples were taken approximately 50m above the borehole at Tanllwyth Bridge and the downstream samples 20m below, at Tanllwyth Flume. Samples were taken each day except on 9 February 1996 when the stream could not be reached due to heavy snowfalls (Table 3).

The third programme was from 2–8 July 1996, during, and prior to which, there were several rainfall events (Table 4). The Tanllwyth was monitored at both sites every three hours, together with the Hafren, which was sampled automatically every three hours during the day (Locks, 1996). As previous work had shown that the

Table 3. Summary of Tanllwyth daily stream chemistry for Programme 2 (8 Jan 96—11 Feb 96). Tanllwyth Flume is downstream of the discrete groundwater inflow and Tanllwyth Bridge is upstream.

Solute	MAXIMUM Tan Flume	Tan Bridge	MINIMUM Tan Flume	Tan Bridge	RANGE Tan Flume	Tan Bridge	MEAN Tan Flume	Tan Bridge
PH	7.34	6.48	4.20	4.17	3.14	2.31	6.30	5.50
Cond (μS/cm)	93.8	97.2	50.6	51.7	43.2	45.5	69.3	56.8
Ca (mg/l)	8.87	4.11	1.55	0.98	7.33	3.13	5.02	2.70
Mg (mg/l)	3.42	2.20	1.28	1.11	2.14	1.09	2.35	1.57
Li (mg/l)	0.0057	0.0033	0.00	0.00	0.0057	0.0033	0.0029	0.0002
Na (mg/l)	6.10	5.86	4.44	4.36	1.65	1.49	5.24	4.81
K (mg/l)	0.53	0.43	0.17	0.14	0.36	0.29	0.32	0.19
SO$_4$ (mg/l)	12.14	12.31	5.76	5.78	6.38	6.53	6.36	6.48
Cl (mg/l)	9.76	9.58	6.69	6.72	3.07	2.85	7.65	7.60
Br (mg/l)	0.025	0.024	0.011	0.01	0.014	0.014	0.018	0.017
NO$_3$ (mg/l)	1.238	1.276	0.518	0.578	0.72	0.698	0.775	0.820
PO$_4$ (mg/l)	0.074	0.014	0.00	0.00	0.074	0.014	0.007	0.004
Al (mg/l)	0.783	0.822	0.008	0.014	0.775	0.808	0.179	0.251
NH$_4$ (mg/l)	0.218	0.215	0.00	0.013	0.218	0.202	0.050	0.050

ephemeral streams did not vary considerably in their chemistry during events, only four samples were taken from Tan North and five from Tan South during the period 2–8 July. SE1 and SE3, which flow perennially, were sampled every three hours initially, but this was soon reduced to twice daily. 15-minute flow data from the flumes on the Tanllwyth and the Hafren were available throughout the storm sampling periods, although discharge measurements were not available for the four first order streams.

Chemical Analysis

During 1995, samples were collected in 60ml square plastic bottles for the first two months of study and subsequently, for the rest of Programmes 1 and 2, in 250ml bottles to provide a larger volume for analysis. These were stored in refrigerators until being taken to ITE Bangor, where the pH and conductivity were measured on all samples immediately on arrival. A subset of samples was chosen subsequently for further analysis, so that detailed chemical data were available for the event periods, as specified in Table 1. These were filtered through 0.45(m nitrocellulose membrane filters and analysed for the 'major' cations and anions (Na, K, Mg, Ca, NH_4 as NH_4-N, Cl, NO_3 as NO_3-N and SO_4) by ion chromatography using a Dionex ion chromatograph. Lithium, bromide and phosphate ion concentrations were also obtained by this method. Aluminium concentrations were analysed using the catechol violet method of Dougan and Wilson (1974) for samples of large enough volume.

For programme 3, all samples were subjected to full chemical analysis. The pH and conductivity were measured in the laboratory at Plynlimon on the evening of collection using standard electrodes. Alkalinity was determined by Gran titration using a Mettler auto-titrator, within one week of collection, using 100ml of sample. Samples were stored at 5°C prior to further analysis at ITE Bangor. Sodium and K were determined by flame emission and Ca, Mg, Fe and Mn by flame atomic absorption spectrophotometry using a Perkin-Elmer model 280 AAS. To suppress chemical interference, Ca and Mg were diluted with lanthanum chloride in a 1:1 ratio before analysis. Ammonium and the anions SO_4, Cl, NO_3-N and PO_4-P were analysed by ion chromatography using a Dionex 2000i system. Silicon and DOC was determined following a UV digestion procedure and colorimetric detection. Silicon was analysed by the standard molybdenum blue method. Aluminium, Pb and Zn were determined by atomic absorption spectrophometry on Thermo-Jarrel Ash Video IIE AAS using a graphite furnace atomizer.

Sampling of soils in the SE3 catchment was also undertaken (Alexander, 1997) to compare soil water pH with drainage ditch pH, to see if the latter could be used as a representative spatially integrated measure of the former and to help identify hydrological pathways. Soil samples with a mass of 50g were taken from each horizon and then spun three times in a centrifuge, to provide enough soil solution for analysis and recording of pH.

Table 4. Chemistry of the seven sites during Programme 3 (2–8 July 1996). F=Forested site, H=harvested site, P=Podzol soil, G=Gley soil.

Solute	SE3 (F P)		SE1 (H P)		Tan North (F G)		Tan South (H G)		Hafren		Tan Flume (downstream)		Tan Bridge (upstream)	
	MAX	MIN	MAX	MIN	MAX	MIN	MAX	MIN	MAX	MIN	MAX	MIN	MAX	MIN
pH	6.36	5.94	6.49	6.28	3.88	3.81	4.25	4.06	6.22	5.22	7.00	5.28	6.55	4.74
Cond (µS/cm)	105.4	56.3	70.4	66.9	99.5	77	79.9	64.8	37.8	34.6	71.2	45.3	48.9	43.3
Ca (mg/l)	6.94	2.98	3.22	2.88	0.42	0.28	0.54	0.34	1.18	0.92	4.82	1.72	2.3	1.42
Mg (mg/l)	3.18	1.5	1.64	1.44	0.94	0.7	0.68	0.54	0.76	0.66	2.12	1.04	1.38	0.9
Na (mg/l)	4.75	4.1	6.57	6.1	5.15	3.81	5.03	4.79	3.96	3.5	5.06	4.08	4.56	3.95
K (mg/l)	0.38	0.14	0.60	0.35	0.07	0.01	2.79	1.61	0.20	0.10	0.54	0.29	0.46	0.18
Si (mg/l)	2.5	1.9	2.2	1.7	1.3	0.6	1.2	0.9	1.6	1.1	2.2	1.3	2.0	1.2
Alk (µeq/l)	48.4	28.8	69.1	46.8	−155.3	−189.5	−74.9	−104.1	22.3	0.2	312.6	6.1	53.7	−16.7
SO_4 (mg/l)	34.08	11.06	8.09	7.28	9.25	5.26	6.61	6.29	4.42	3.76	6.59	5.58	6.69	5.71
Cl (mg/l)	7.25	5.15	11.80	10.48	8.09	5.28	7.60	5.37	6.23	5.30	7.23	6.12	7.23	6.08
NO_3 (mg/l)	2.08	1.42	4.87	2.74	0.13	0.04	1.11	0.4	1.24	0.58	3.23	1.33	3.5	1.55
PH_4 (mg/l)	0.18	0.00	0.09	0.00	0.06	0.00	0.06	0.00	0.06	0.00	0.12	0.00	0.03	0.00
DOC(mg/l)	1.8	0.7	5.4	1.0	37.8	23.6	37.5	20.9	7.3	2.1	12.7	2.8	11.5	2.6
Fe (mg/l)	0.06	0.00	0.16	0.07	0.86	0.53	1.60	1.19	0.22	0.07	0.46	0.17	0.42	0.10
Al (mg/l)	0.038	0.015	0.139	0.036	0.685	0.490	0.963	0.718	0.290	0.075	0.454	0.129	0.502	0.092
Mn (mg/l)	0.20	0.00	0.01	0.00	0.02	0.01	0.04	0.01	0.04	0.00	0.13	0.09	0.13	0.07
NH_4 (mg/l)	0.04	0.00	0.06	0.00	0.03	0.02	0.03	0.00	0.15	0.02	0.04	0.00	0.12	0.00
Pb (µg/l)	0.9	0.1	1.7	0.5	2.4	0.8	3.4	1.4	2.1	0.3	1.4	0.2	1.6	0.0
Zn (µg/l)	16.4	4.4	16.3	3.2	15.4	12.4	35.0	19.2	13.5	5.2	54.9	6.3	60.1	8.3

Results

A) SUMMARY OF DATA COLLECTED

A summary of the data collected from all sites during 1995–6 is shown in Tables 2–4. Table 2 shows the daily data for the period of June to September 1995 for all six streams (Tanllwyth Bridge was not sampled). Table 3 shows daily data for both Tanllwyth Flume and Tanllwyth Bridge (above and below the groundwater inflow point) for January to February 1996 and Table 4 summarises data from all seven sampling sites collected during July 1996. A single daily or three-hourly mean value for each solute cannot be meaningfully calculated for Programmes 1 and 3 (Tables 2 and 4), as the data were not continuous throughout the periods of record. From these data, comparisons can be made between the drainage ditch response and main stream response to assess the effect of scale, and to consider the links between soil, ditch and stream chemistry. The influence of soil type can also be investigated by comparing the response of SE1 and SE3, which drain podzols, with Tan North and Tan South, which drain gleys. As one site of each of these pairs had been harvested (SE1 and Tan South), the effect of landuse change can also be considered. Data from above and below the discrete groundwater inflow to the Tanllwyth can be used to assess the influence of base-flow on the overall episodic chemical response. Comparisons can also be made between solutes to identify patterns of hydrochemical changes with flow at different sites.

As the sampling interval differs between Tables 2, 3 and 4, there are limitations in comparing these results directly, but a number of conclusions can be drawn. The majority of solutes have a wider range of values in summer 1995 (Table 2) than in summer 1996 (Table 4), despite the less frequent interval of sampling, probably because the 3-hourly data presented here covered only two small summer storms, which had dry antecedent conditions and a relatively small storm-flow component. In contrast, the 1995 data covered a wider range of storm events, during which some solutes exhibited a significantly larger range in concentration. Had 3-hourly data been available for summer 1995, larger ranges would have been expected.

The rainfall events sampled during July 1996 were small and there was little increase in stream-flow. Evaluation of flow duration curves from 1976 to 1995 showed the peak discharge to be exceeded 29.7% of the time in the Hafren and 17.5% of the time in the Tanllwyth; the difference in these percentages was explained by a double peak in the Hafren, which attenuated the maximum discharge. There were several rainfall events from 24 June to 8 July 1996; with each successive event, a higher discharge occurred as the catchment wetness increased. Although the changes in river discharge were not dramatic, significant changes were noted in the stream chemistry, as the presentation of results from this period shows clearly. The Hafren showed a less 'flashy' response than the Tanllwyth during all

events monitored, the larger drainage area and more permeable soils in the former probably causing greater attenuation of the flow peak.

B) EFFECTS OF SCALE

i. Main Features of the Ditch Response

Tan North and Tan South were ephemeral, flowing only during storm events (no groundwater component was evident due to the presence of an impermeable clay layer). These sites were the most acidic of those monitored, with very little range in pH (3.8 to 5.0) as shown in Tables 2 and 4. These sites had distinctively low Ca, Mg, NH_4, K and NO_3 ion concentrations and high Al concentrations compared to other sites. Table 2 shows a larger range of values than Table 4, due to the longer sampling period of Programme 1 compared to Programme 3, indicating the influence of season and antecedent conditions. Ranges were still small compared to other streams, however. The high acidity and presence of organics for these ditches explains the increased concentration of the metals Fe, Al, Pb and Zn.

Figure 2(a) shows the very small change in pH in Tan North and Tan South during the event of 14–19 July 1995. Other events showed a similar response. The ditches draining podzolic soils (SE1 and SE3) were perennial, since the more permeable soils produce a base-flow component. They typically had a pH of approximately 6.5 between events, being slightly higher than that observed in the Hafren, but approximately 0.75 units lower than that at Tanllwyth Flume, as illustrated in Fig. 2(a). In comparison to the gley sites, the podzols showed a distinct event response, with a decline in pH of up to 1 unit observed at the daily monitoring frequency, although this drop was not as substantial as that in the Hafren or Tanllwyth. The pH of the podzol sites was approximately two units higher than for the gleys (Tables 2 and 4, Fig. 2(a)).

The results of the soil samples taken from five soil pits in the SE3 catchment during January 1996 are given in Table 5. These gave an average A horizon soil-water pH of approximately 4.5 and a B horizon soil-water pH of approximately 5.2 and may be used to indicate the link between observed ditch chemistry and soil chemistry. SE1 and SE3 had stream-water pH values, which, during storm events, tended toward those of the sampled soil-waters (Fig. 2(a)). This suggested that, at these times, soil-water was the main component of flow. At other times, it appeared that there was a higher pH water source, probably a deeper subsurface component of stream-flow.

Ditch conductivities may also be used to compare storm responses. In contrast to the pH response, SE1 and SE3 did not vary much during events, but Tan North and Tan South conductivities were more dynamic (Fig. 2(b)). Flow in the ephemeral gley streams began with a high conductivity flush, before settling down to more constant values
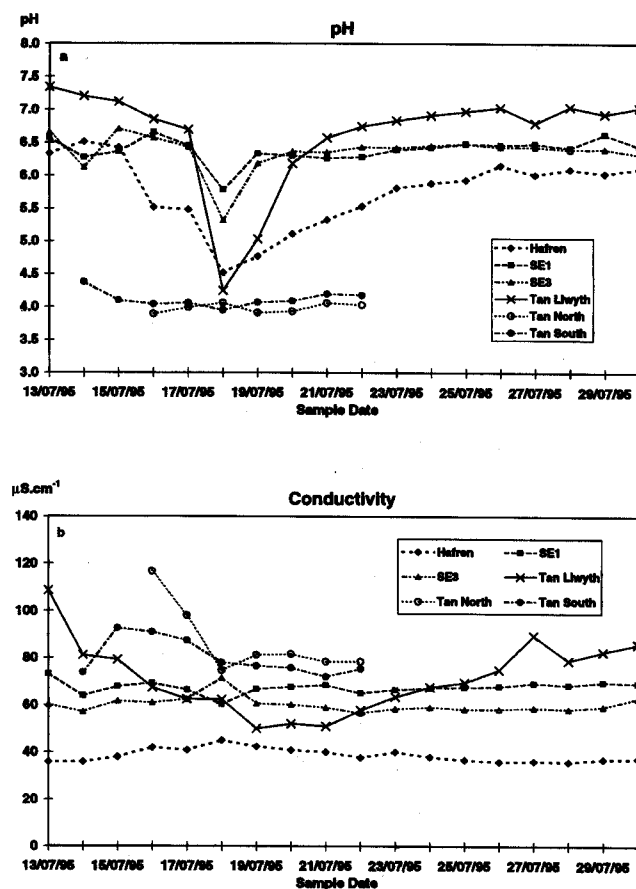
Fig. 2. *Daily streamwater pH and conductivity plots for 13 July to 30 July 1995 (under Programme 1) for all six streams. The flume site 6 is shown for the Tanllwyth.*

Table 5. Soil-water pHs from the five pits in the SE3 catchment, taken January 1996.

Pit	Horizon	pH value
1	A	4.83
1	B	5.47
2	A	4.18
2	Black	4.33
2	Brown/Yellow	5.46
2	Grey	4.97
3	A	4.88
3	B	5.19
4	A	4.57
4	B	5.13
5	A	4.24
5	B	5.02
5	wet/black	5.18
	average A	4.51
	average B	5.20

(Fig. 2(b)). Overall, the pH and conductivity data showed that Tan North and Tan South had a chemical response that reflected mainly a soils contribution, whereas SE1 and SE3 showed a two component response, even during low flow conditions. Neal *et al.* (1997c) also concluded from ANC measurements of these ephemeral streams that those draining impermeable gley soils were supplied mainly with water from the soil zone and were of fairly uniform chemistry, whereas those associated with free-draining podzols combined at least one soil and one ground-water component and had greater chemical variation through the year.

Calcium and magnesium are weathering components, indicative of base-flow. A very similar response was seen for both ions for different streams and events, except that Ca concentrations were approximately double those for Mg. Figure 3 shows a typical event response for Ca from the event of 14–19 July 1995. The lowest concentrations were recorded in the ephemeral gley streams, Tan North and Tan South, as would be expected because of the absence of a base-flow component. Tan North and Tan South had the lowest concentrations of all the streams during events, but during the storm of July 1995, began with a high Ca and Mg flush. Concentrations were initially similar to those of SE1 and SE3, but dropped rapidly, as the contribution of water from upper horizons increased as was also shown by the conductivity data (Fig. 2(b)). This was however, not so evident during September 1995, when antecedent conditions were wetter. SE1 and SE3 also showed a decrease during events, but of a smaller magnitude, implying a larger component from deeper, well drained soils.

Tan North and Tan South showed the highest Al concentrations of all streams (Tables 2 and 4), indicating a predominant water source from the upper soil horizons. These again showed a higher concentration at the start of an event, which would have contained seepage from the soil where high soil-water concentrations of aluminium had accumulated (Fig. 4). The depletion of Al for Tan North is not seen at Tan South and is the opposite response to that seen in the other streams. These all had very low concentrations during base-flow, which increased rapidly during events. SE1 and SE3 generally had lower Al concentrations than the main streams, supporting the hypothesis of a base-flow component entering these ditches.

In comparison to the Hafren, SE1 and SE3 had higher values of Ca, Mg, Na, Cl and SO_4 and lower NH_4, NO_3 and Al (Tables 2 and 4). The generally lower ammonium, potassium and nitrate ion concentrations in the small streams suggested that these were less affected by biological processes than the Hafren.

The effect of soil type on the flow pathways and chemistry can be considered by comparing the responses between the two pairs of ditches. Alkalinity, Si, Ca and Mg were all lower on the gleyed sites than the podzols (Tables 2 and 4), reflecting the absence of water from

lower horizons. Na and SO_4 concentrations showed no significant differences between soil types, although nitrate concentrations were much lower on gleys, which could reflect denitrification processes. Concentrations of DOC, Fe, Al, Zn, and Pb were all higher in the gleyed soil streams, reflecting a source from organic surface horizons. Hence, the differences in flow pathways through the soil during storms were responsible for different stream chemistries.

The effects of land-use may also be considered by comparing the forested with the harvested site on each of the two soil types, i.e. by comparing Tan North with Tan South and SE3 with SE1 respectively. The pH was higher for the harvested site compared to the forested site on the same soil (Table 4). SE1 also responded to smaller events than SE3, which, for example, showed little variation in aluminium in response to rainfall on 30 July 1995 and 1 August 1995 (Fig. 4). This showed that the forested site (SE3) probably allowed less precipitation to reach the stream, because of interception or evaporation. When this stream did respond, however, the Al concentrations peaked at higher values than in SE1, which was being harvested during 1995. In contrast, on the gley soils, Tan South always had higher aluminium concentrations than Tan North; the felling that was taking place in the catchment causes mobilisation of Fe and Al from the upper soil horizon, primarily by increasing DOC concentrations in the soil-water (Hughes et al., 1990).

Na and Cl were higher in the harvested catchments compared to the forested ones (Table 4); however, the reverse pattern was observed for the other atmospherically scavenged elements of Ca, Mg, and SO_4. Higher nutrient concentrations were observed at the felled sites due to decomposition processes. The generally lower ammonium, potassium and nitrate ion concentrations in the small streams suggested that these were less affected by biological processes than the Hafren.

ii. Main Stream Response

The responses between the main stream and the drainage ditches may be compared to consider the effects of scale, especially between the Hafren, SE1 and SE3 as these all drained podzols and were perennial. Comparisons may also be made between the two main streams, which are fed by tributaries with different flow regimes.

The Tanllwyth Flume showed a more rapid and dramatic hydrochemical response than the Hafren to rainfall events, because of the smaller catchment area and less permeable catchment soils. Ion concentrations and conductivity changes also occurred with smaller events in the Tanllwyth than in the Hafren, where, for example during Programme 1 (1995), ion concentration changes occurred only during the larger events in July and at the end of September (aluminium was the only exception to this).

Both main streams responded to all monitored events with pH depressions and, between events, the pH at Tanllwyth Flume was consistently about one pH unit higher than in the Hafren. A wider range of values was also observed in the Tanllwyth; although conductivity and pH were initially higher at Tanllwyth Flume, both values dropped to be similar to those observed in the Hafren during events. Fig. 2(a) shows that during the storm period of 14–19 July 1995, the pH at Tanllwyth Flume dropped below that observed in the Hafren to values nearing those recorded in Tan North and Tan South. Several such ditches, draining gley soils, flow into the Tanllwyth and it is likely that, during events, such sources of water dominate the main stream response.

Monitoring in Programme 3 (July 1996) with a sampling interval of three hours, allowed more detailed analysis of the timing of these chemical changes. Figure 5 shows that the pH depressions did not, in fact, coincide with the time of peak discharge, but occurred three to six hours later. In comparison to the Tanllwyth, the tributaries of the Hafren drain mainly podzols, as do SE1 and SE3. As the pH in the Hafren falls below that in these streams, it may be hypothesised that a source of soil water is still entering the Hafren during events, possibly directly or via other tributaries. The middle section of this stream flows over gley soils, which is a probable source of low pH water.

During conductivity depressions, the Tanllwyth responded earlier than the ephemeral drainage ditches, Fig. 2(b). The extent and magnitude of the decrease varied between events. Unlike the pH response, for which the two main streams reacted similarly to changes in flow, the Hafren showed little change in conductivity during events, compared to the Tanllwyth (Figs. 2(b), 5(b)). It is evident that the low-flow chemistry has an effect on the magnitude of the event response in each stream.

Ca and Mg ion concentrations also fell during periods of rainfall, as their source is alkaline base-flow diluted at these times by storm event water from upper soil horizons. Ca and Mg affect the conductivity directly, explaining the similar responses recorded. The Tanllwyth Flume site showed the highest concentrations of Ca and Mg and the greatest range in values of all streams (Fig. 4, Tables 2–4). During events, concentrations at this site fell to below those recorded in SE1 and SE3, which had the second highest concentrations prior to rainfall. A full explanation of the dramatic changes seen at Tanllwyth Flume requires evaluation of the groundwater inflow on the episodic response. However, it can be seen from Fig. 3 that the Ca concentrations at Tanllwyth Flume tend towards those recorded in Tan North and Tan South, supporting the hypothesis that the storm response of Tanllwyth Flume is dominated by tributary and soil-water inflow, which have very low concentrations of Ca and Mg once flow has initialised. SE1 and SE3, together with the Hafren, showed less variation than the Tanllwyth, and the Hafren has concentrations about half of those in the podzol drainage ditches.
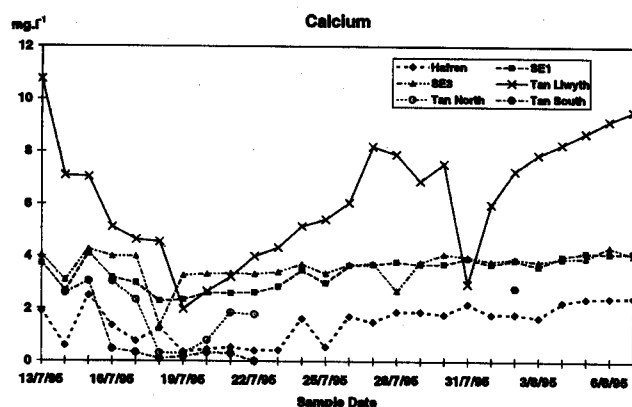
Fig. 3. *Daily calcium ion concentrations for the six streams for 13 July to 8 August 1995 (under Programme 1). The flume site is shown for the Tanllwyth.*

The influence of soil-water inflow to the main streams via drainage ditches can also be seen from the aluminium response. Concentrations in both main streams increased with increasing flows, however, this varied with the magnitude of the event. For the large events during Programme 1 in July 1995 (Fig. 4) and at the end of September 1995, Al concentrations rose dramatically. However, for the event at the beginning of September, the concentrations showed little difference from those at base-flow. Both main streams responded over the same time-period, and concentrations were lower in the Hafren than the Tanllwyth.

The large peaks in aluminium concentrations in the Hafren and Tanllwyth tended towards values recorded in Tan North and Tan South, and in fact, peaked above them (Fig. 4). This suggests the importance of inflow from upper horizons and drainage ditches, although the daily monitoring is unlikely to capture the dynamic range of the ditch responses.

For Programme 3, during the 1996 summer period, Si, Cl, and Na concentrations in the Hafren, although small
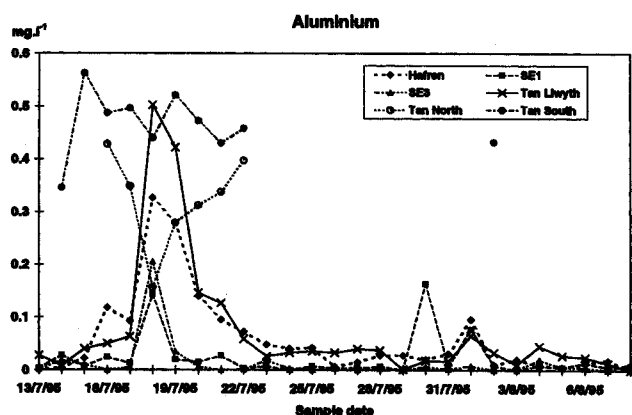

Fig. 4. *Daily aluminium ion concentrations for the six streams for 13 July 1995 to 8 August 1995 (under Programme 1). The flume site is shown for the Tanllwyth.*

in range, showed dilution during storms. DOC, Al, K, Fe, Mn and Zn all showed an increase just after a storm event, indicative of waters from surface organic horizons. However, during Programme 1 (1995), Na and Cl ions showed no discernible variation with flow, the variation seen for Cl and Na in July 1996 probably not being picked up from daily data. It appears that atmospheric inputs of these ions did not affect the stream chemistry directly. Sulphate ion concentrations increased slightly with flow in both main streams, but soon decreased to pre-event conditions. Potassium ion concentrations, however, showed little variation with flow.

Nitrate concentrations increased in both streams in 1995 with increasing flow, and were much higher in the Tanllwyth than the Hafren. Nitrate concentrations in the Tanllwyth also took longer to return to base-flow values, except between the September storms. During the resulting events, nitrate concentrations remained higher than those did before the rainfall, due to the catchment remaining wet after the precipitation in early September 1995. The same response was seen after the event in late September 1995. During July 1996, NO_3 appeared to show a clearer nutrient response in the Hafren than was observed in the Tanllwyth, with peak values clearly lagging behind flow. The actual values varied between 0.6 and 1.2 mg/l, such low concentrations being typical of summer.

c) Effect of Point Groundwater Inflow to the Tanllwyth

Figure 5 clearly shows the effect of the groundwater inflow on the episodic chemistry of the Tanllwyth. The pH response upstream of the borehole, at Tanllwyth Bridge, and downstream of the borehole, at Tanllwyth Flume, showed a similar pattern, with a consistent difference of approximately 0.5 units between the two sites. The lowest pH values were recorded between three and six hours after peak flow and then recovered towards pre-event values, but more slowly than they declined.

Conductivity and alkalinity both showed a similar response, with a decrease during events, again beginning to recover a few hours after the flow peak (Fig. 5(b)). However, values downstream of the borehole, although initially much higher than those upstream, dropped dramatically during the events to reach values nearly as low as those recorded upstream, where only a small decrease occurred. This was indicative of storm event water diluting the base-cation rich stream-water during events. The effect was more pronounced downstream of the borehole, because base cation concentrations were very high during low flow periods due to the alkaline groundwater inflow. During events, this base-flow component chemical signature was over-ridden by that of storm-flow, dominated by acidic soil and ditch-water.

Figure 6 shows the dilution of Ca during episodes at both sites (Mg showed a very similar response), as the chemistry of the storm-event water dominated the
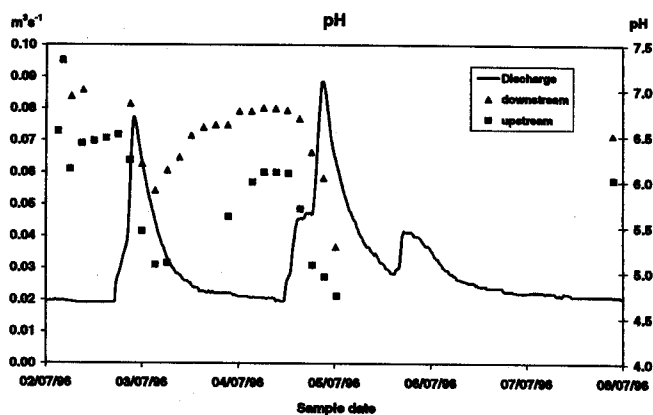
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Fig. 5. *Tanllwyth pH and conductivity in response to storms from 13:00hrs, 2 July to 13:00hrs, 8 July 1996 (under Programme 3). The flume site is located downstream of the discrete groundwater inflow and the bridge site is upstream.*

Fig. 6. *Calcium ion concentrations in the Tanllwyth during storm events from 13:00hrs, 2 July to 13:00hrs, 8 July 1996 (under Programme 3). The flume site is located downstream of the discrete groundwater inflow and the bridge site is upstream.*

response, with Al returning more slowly to pre-event levels than at Tanllwyth Flume. Three-hourly data from the summer sampling during 1996 showed the reverse to be true, however, with a wider range of values and a more rapid response being seen at Tanllwyth Flume. Although these differences cannot be explained, it is clear that Al showed a good correlation with flow, even if it was more damped at some locations at certain times. This fits with the theory of high concentrations of Al entering the stream during events from upper soil horizons and can be correlated with the high Al concentrations recorded in the ephemeral gley streams.

response. Concentrations during events were seen from the data from Programme 1 to tend towards concentrations seen at Tan North and Tan South, indicative of the soil water component at these times (Fig. 3). Although dilution was seen at both Tanllwyth Flume and Tanllwyth Bridge, it was far more marked at the flume (Fig. 6), where concentrations fell to values nearly as low as those upstream of the borehole, despite the much higher pre-event concentrations downstream. As the event passed, concentrations rose again at a slightly less rapid rate than they fell. Daily Ca data from early 1996 (Fig. 7) show a longer term dynamic recovery of Ca, and to higher concentrations, below the borehole than above, following the event response. These then declined during the next event, clearly showing the effect of dilution of base-flow chemistry by incoming soil and drainage-ditch water.

The groundwater inflow to the bed of the Tanllwyth appeared to have little effect on Al concentrations at low flows, with concentrations recorded both above and below the borehole being very similar. During events, it was difficult to identify a pattern from the available data. Daily data from January 1996 (Fig. 8) showed the upper sampling location (Tanllwyth Bridge) to have a more damped
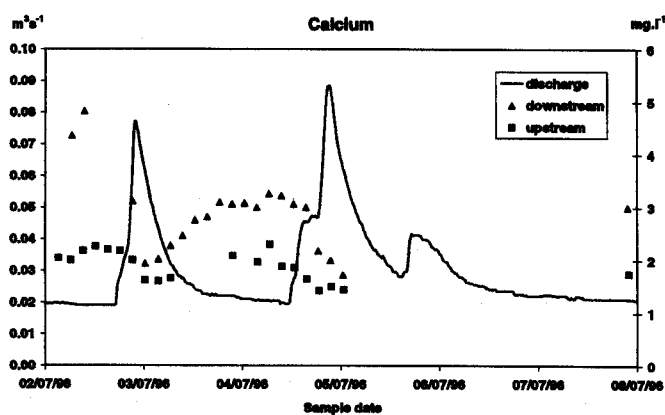

Fig. 7. *Daily calcium ion concentrations in the Tanllwyth from 8 January to 11 February 1996 (under Programme 2). A sampling time of 09:00hrs has been assumed for these daily samples. The flume site is located downstream of the discrete groundwater inflow and the bridge site is upstream.*

Discussion

Robson *et al.* (1993) suggested that 'Piston flow' takes place at Plynlimon, whereby, except for large events, much
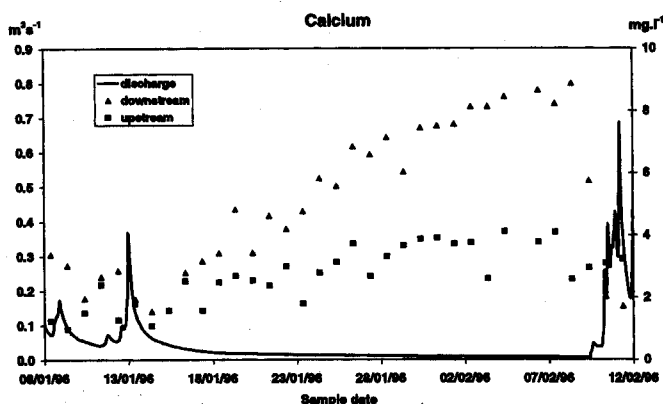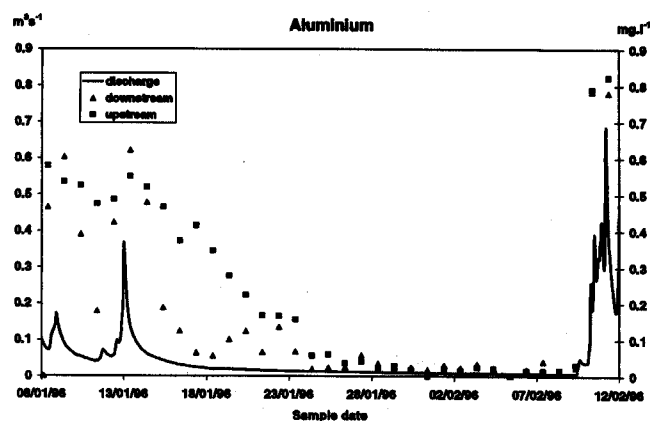
Fig. 8. *Daily aluminium ion concentrations in the Tanllwyth from 8 January to 11 February 1996 (under Programme 2). A sampling time of 09:00hrs has been assumed for these daily samples. The flume site is located downstream of the discrete groundwater inflow and the bridge site is upstream.*

of the rainwater remains in the catchment and is transferred to the stream by successive episodes. Their study found the pH response of the Hafren forest streams to be related to flow and unaffected by short-term variations in rainfall pH and conductivity. Conductivity was related to flow but was also affected by the rainfall chemistry of previous events. Rainwater pH was rapidly affected by in-catchment processes, particularly cation exchange in the soil. Results presented in this paper have also shown pH and conductivity to be largely controlled by discharge and hydrological pathways, and have illustrated a scale-dependent and soil-dependent stream response.

The gley soils of Tan North and Tan South gave rise to ephemeral first-order streams, dominated by acidic aluminium-rich soil waters. In contrast, the first-order streams SE1 and SE3, which drained podzols, could not be represented by a single source of water; their stream-water could be thought of as a mixture of soil and groundwater sources. Measurements of water chemistry in both shallow (up to 20m) and deep (greater than 50m) boreholes in the Upper Severn catchments showed groundwater ANC to alter considerably both spatially and temporally (Hill and Neal, 1997). The spatial changes were unrelated to the borehole location down-slope. However, the ANC was generally higher than in the ephemeral streams and alkalinity was usually found to be greater in the deep boreholes. This can explain the chemical variations observed in SE1 and SE3 stream-water, which will be affected both by the changing percentage of groundwater inflow and its chemistry.

For the larger catchments, the Hafren and Tanllwyth, an increased influence of groundwaters was apparent, and, in particular, the discrete groundwater input was a source of alkaline and base cation-rich water with a higher pH and conductivity than the storm event water. This was responsible for the higher pH and conductivity values seen at the

Tanllwyth Flume in comparison to the other streams and at Tanllwyth Bridge, except during storm events. Unlike the Hafren stream where base cation concentrations remained relatively constant throughout low flow periods, base cation concentrations in the Tanllwyth increased steadily between events, suggesting either a slow response of base-rich water or a slow decline of acidic inflows.

Monitoring stream water chemistry at the two sites on the Tanllwyth meant that the differences in chemistry could be attributed to the discrete groundwater input. These results also showed the dominant effect of drainage ditch and soil-water inflow during events, lowering pH and base-cation concentrations and increasing Al. The groundwater source did not act as a buffer against the pH falling in the Tanllwyth as might have been expected. Indeed, during storm events the daily data showed pH values to fall to lower values than in the neighbouring Hafren and aluminium concentrations to be higher. This was a result of the overriding effect of inflow from the ephemeral streams that discharged into the Tanllwyth. Monitoring of Tan North and Tan South showed that, as these drain acidic and aluminium-rich gleyed soils, their stream water chemistry was similar to that which would be expected from soil water. The influence of this acid water at storm-flow appeared to be large enough to override the groundwater influence on the stream water chemistry, i.e. the groundwater input to the Tanllwyth appeared to be too small to have a significant effect on chemistry at high flows.

Evaluation of the episodic response of the other streams has also implied that, during storm events, the main stream response is dominated by an acidic soil-water component of inflow from tributaries. However, Hill and Neal (1997) found no significant longitudinal change in pH or alkalinity in the main channels as a result of small stream acidic input. The apparent discrepancy in these conclusions could be a result of the weekly sampling interval used by Hill and Neal, as opposed to observing the episodic storm response.

The atmospherically scavenged elements, Na and Cl, were higher during the storm period of 1996 at the felled catchments, which may reflect a flushing of accumulated solutes before any decrease occurred, as harvesting had only recently taken place. Na and Cl are normally higher in streams under forest as a result of scavenging. This has been shown to be the case at Plynlimon, by comparing base-flow chemistry at sites in the Hafren forest with grassland sites from the Wye catchment headwaters at Plynlimon (Locks 1996). However, the reverse results were seen for the July 1996 period for Mg and SO_4, which were higher on the forested podzol site.

Generally, concentrations of nutrients (NO_3, PO_4, NH_4 and K) were very low in summer, as expected, because of biological uptake. Under storm-flow conditions, NO_3 concentrations increased with discharge, usually immediately following the storm peak. The higher values at felled sites

can be explained by decomposition and the more favourable conditions for microbes causing mineralisation. Removal of shade following felling would result in higher soil temperatures, creating conditions more favourable for decomposition and mineralisation.

Other nutrients and trace metals associated with the organic layer also increased with discharge. Additionally, they were observed to increase at the clearfelled sites compared to the forested sites, due to decomposition and land disturbance, which caused a surge in biological activity. During storm events, DOC showed a very distinct rise in concentration, shortly following the discharge peak. This coincided with increases in Fe and Al concentrations in both the Hafren and Tanllwyth. Aluminium is toxic to many species and its concentration is directly related to the acidity of the water, although inorganic aluminium speciation varies with pH and the presence of other elements. Hughes *et al.* (1990) claim that DOC determines the chemistry, solubility and transport of Al and Fe in the O horizon, and it appears that the rise in Al at Plynlimon was of organic form. However, as only total Al was measured, this could not be assessed. This showed how, during storm conditions, the contribution of the shallow organic soil horizons increased. Inorganic aluminium concentrations tend to be higher in storm-flow than base-flow, as the water is derived from the more acidic, aluminium bearing upper soil zones (Neal *et al.*, 1992b).

Conclusions

Monitoring of the episodic hydrochemical response of streams in the Upper Severn catchment, at daily and three-hourly sampling intervals, has shown that hydrological flow pathways clearly influence the stream chemistry. During storm events, the contribution of water from the surface organic horizons increased, causing a pH and alkalinity depression, coinciding with dilution of the weathering components of Ca, Mg and Si. This was mirrored by the rise of the nutrients DOC, K and NO_3, together with metals complexed by organic acids (Al, Fe, Zn and Mn). The effects of scale and soil-type were also considered, by sampling two first-order ditches draining gley soils and two draining podzols. The two draining gley soils showed little chemical variation because the base-flow component was restricted by an impermeable clay layer, which left only the organic surface horizons as a source of water and caused the flow to be ephemeral. In contrast, those on podzols received a groundwater component, which increased stream alkalinity and enabled perennial flow.

The chemistry of the major streams, the Hafren and Tanllwyth, was intermediate between that of the first order ditches draining gleys and podzols, reflecting the mixture of contributing sources. These main streams showed the greatest variation in pH and alkalinity while gleyed ditches showed little change and the podzol ditches appeared to be groundwater buffered. Forestry affected chemistry by

atmospheric scavenging and evaporation and recently felled sites showed a flushing of some elements and the influence of biological processes from decomposition.

The anthropogenically initiated point groundwater inflow to the second-order Tanllwyth had previously been shown to improve stream chemistry significantly by increasing ANC and base cation concentrations (Neal *et al.*, 1997a,b). However, the use of detailed episodic data has revealed that, although this was the case at low flows, the effect of low pH, high aluminium soil water, entering the stream from ephemeral channels during storm events, overrode the influence of the groundwater source. Hence, the Tanllwyth had a wider range of pH, alkalinity and cation concentration values after initiation of the groundwater inflow to the streambed, which may represent degradation in the ecological environment. This could bring into question the development of such groundwater inflows for remediation.

The high temporal resolution data presented here provide clear insights to the spatio-temporal variability of hydrological and hydrochemical responses. Observations from streams at different scales have shown the episodic response to be dependent on hydrological pathways, soil type, land-use and groundwater inflow. However, past work has revealed that the chemistry does not necessarily respond in the same way to different storms and antecedent conditions (Chapman, 1994); it is, therefore vital that more storm events are sampled at a high frequency. Monitoring of larger events and those in different seasons would help to improve modelling of the effects of land-use change and pollution. Such an expansion and extension of the existing database is fundamental to assessing the effect of national environmental policies.

Acknowledgements

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