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Hydrology & Earth System Sciences

The water quality of streams draining a plantation forest on gley soils: the Nant Tanllwyth, Plynlimon mid-Wales

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Abstract

The water quality of the Nant Tanllwyth stream in the Plynlimon region of mid-Wales is related to the key hydrobiogeological controls and the effects of conifer harvesting based on an analysis of rain, cloud, stream and groundwater measurements. The results show the normal patterns of stream water quality response to hydrology. Thus, there is a high damping of atmospheric inputs due to storage in a highly heterogeneous soil and groundwater system. Correspondingly, there is a highly dynamic response for components such as calcium, bicarbonate and aluminium. This response links to the relative inputs of acidic and aluminium-bearing soil waters under high flow conditions and base enriched bicarbonate bearing waters from the groundwater areas under baseflow conditions. The introduction of a deep borehole near the main stem of the river opened up a groundwater flow route to the stream and other parts of the catchment. There were two aspects to this. Firstly, it caused a change to the stream water quality, particularly under baseflow conditions, by increasing the concentrations of calcium and magnesium and by reducing the acidity. The monitoring shows that this change has persisted for over eight years and that there is no sign of reversion to pre-borehole times. Secondly, it caused a change in the groundwater level and chemistry at a borehole on the other side of the river. This feature shows that the fracture system is of hydrogeochemical and hydrogeological complexity. The effects of conifer harvesting are remarkable. At the local scale, felling leads to the expected short term increase in nitrate, ammonium and phosphate from the disturbance of the soil and the reduction in uptake into the vegetation. Correspondingly, there is a reduction in sodium and chloride linked to reduced scavenging of atmospheric inputs from cloud water by the vegetation and also due to increased dilution potential due to reductions in transpiration by the trees. However, within the main stream, virtually no change is observed in stream water quality with felling, except for a decrease rather than an expected increase in nitrate concentration. It seems that the increase in phosphate, for a system that is essentially phosphate limiting, has stimulated biological activity in the stream leading to increased uptake of nitrate and ammonium. However, there is little change in the sodium and chloride in the stream and there are important issues of the representative nature of studying small scale drainage areas. Boreholes, introduced to assess the impacts of the felling programme, show unexpected variations in groundwater chemistry. These variations are associated with the complexity of both flow routing and the chemical reactivity within the groundwater and lower soil zones, rather than changes that can be linked specifically to felling. The implications of the study are discussed in relation to both process understanding and forestry management practices.

Keywords: water quality, acidification, conifer, harvesting, pH, nitrate, ammonium, phosphate, nutrients, alkalinity, Plynlimon, Wales, Tanllwyth, streams, groundwater

Introduction

An important environmental concern for the UK uplands relates to one of the major forms of historically recent land-use change, the introduction of extensive plantations of exotic conifers (e.g. Sitka spruce, Lodgepole pine, Douglas Fir) onto acidic and acid sensitive soils between the 1920s and 1960s. These plantations have now reached maturity and are being felled or are being replanted for second or subsequent rotations (Hudson *et al.*, 1997a). There has been a major impetus for stream water quality monitoring to determine the impacts of forest development and forest harvesting (e.g. Stoner and Gee, 1985; Harriman *et al.,* 1994; Neal and Reynolds, 1998). In terms of felling, recent results have shown that while there can be deteriorations in water

quality, the impacts are often of little practical concern at the catchment scale due to the site management policies adopted by the forest industry to maintain and improve the environment (Neal *et al.*, 1998a,b; FC, 1993).

The results of a study of the water quality changes following conifer harvesting are described for a site within the Plynlimon experimental catchments of the Centre for Ecology and Hydrology (CEH) in mid-Wales, the Nant Tanllwyth. The catchment has stagno-humic gley soils, a situation where the worst environmental impacts might be expected given:

- The soils are highly acidic (with soil pH values (in water) throughout the profile of around 4.0 and base saturation values of around 10%) and aluminium bearing, and soil perturbations might lead to greater stream acidity;
- The soils are highly reducing and so soil disturbance may lead to releases of iron, reduced forms of nitrogen (ammonium in particular) and phosphorus to the streams which can be environmentally harmful;
- The soils are of low permeability and hence there is greater risk of the discharge of acidic and nutrient-rich soil water to the streams during rainfall events.

The information presented in this paper complements other studies of conifer harvesting at Plynlimon and other parts of Wales that deal with felling responses for podzolic soils (Reynolds *et al.*, 1988; Stevens *et al.*, 1988; Neal *et al.*, 1992a,b, 2003a) and brown earth soils (Neal *et al.*, 1997a, 2003b), thereby infilling information to cover all the major soil types for the region. The data also show that even for catchments with soils that have a high potential for water quality deterioration, the impacts of felling on stream water quality can be minimal.

Study area

The study area is part of the headwaters of the River Severn. The Nant Tanllwyth drains into the Afon Hafren (the Welsh name for the River Severn) near its confluence with the other main tributary of the upper River Severn, the Afon Hore. The Afon Hafren and the Afon Hore drain a hill top plateau dominated by acid moorland in the upper portion of the catchment (Pumlumon Fawr) and the Hafren Forest. The catchment of the Nant Tanllwyth is wedged between these two catchments, such that the top is 'pinched out' and does not extend far onto the upper plateau region. The altitude range for the Nant Tanllwyth is about 335 to 540 m a.s.l. and its catchment area is 0.916 km^2. The Tanllwyth catchment is dominated by thin stagno-humic (peaty) gley soils overlying bedrock comprised of fractured Lower Palaeozoic mudstones, shales and grits. The Tanllwyth catchment was planted overall with Sitka spruce (*Picea sitchensis*) in various phases from the mid 1940s through to the late 1960s. About three-quarters of the southern half of the catchment (the southern side of the river channel), was felled in February 1996 where only the tree stem was removed from site leaving the felling debris (stumps, branches and needles) behind. There was also some limited felling during 1993 and 2002.

The sites comprising this study are described below. Further details of the locations of the sites together with other background information are provided in Neal and Kirchner (2000).

Atmospheric inputs

Rainfall is collected weekly from open gauges at the top of the Hafren and bottom of the adjacent Gwy catchment. Cloud-water is collected using a passive lidded 'harp type' system at one site near the top of the catchment on a weekly basis (Wilkinson *et al.*, 1997). Monitoring of rainfall began in 1983 and for cloud-water in September 1990.

Nant Tanllwyth

The main stem of the Nant Tanllwyth was monitored near its confluence with the Hafren. Weekly grab-samples have been collected since September 1991 from a point 10 m upstream of the Tanllwyth flume which is maintained by CEH hydrologists. In May 1994, a deep (95 m) borehole was drilled about 10m to the north and about 10m upstream of the Nant Tanllwyth stream monitoring site (Neal *et al.*, 1997b). This resulted in the opening of blocked fissures in the rock into the stream which released increased quantities of calcium laden groundwaters of high Gran alkalinity. The groundwater input is specifically important under baseflow conditions in terms of chemistry and the change was first noticed the following spring (N.B. in terms of hydrology, the borehole is artesian during wet conditions and the borehole had to be capped to avoid groundwater release to the surface at such times). Because of the influence of the borehole on water quality, the stream monitoring site was relocated 25 m upstream of the borehole. Monitoring at the new location began on 26th September 1995. For the present analysis, the data affected by the introduction of the borehole are excluded from the analysis of the time series (a period from 7th March 1995 to 26th September 1995). However, the effects of the borehole were monitored with continued sampling for pH and Gran alkalinity at the 'upstream' and 'downstream' sites. The 'upstream' data collected after the introduction of the borehole is probably representative of a continuum of the 'downstream' data prior to the introduction

of the borehole (the additional input of water from catchment sources draining into the river between the two monitoring points is insignificant). No monitoring was undertaken between 20th February 2001 and 22nd May 2001 due to an outbreak of 'foot and mouth' disease which ravaged the UK around that time.

Tanllwyth: small stream drainage areas and associated groundwaters

A pair of small sub-catchments, with areas of less than 1ha, was introduced in spring-summer 1994 to examine the interaction between soil type and forest harvesting on water quality. Monitoring of the streams began 28th April 1994 while monitoring of the boreholes began 9th August 1994 (after allowing time for the effects of borehole introduction on water quality to subside). There was one control and one manipulation (harvesting) site located to the north and south of the main stem of the Nant Tanllwyth, respectively. The entire sub-catchment of the manipulated site was clearfelled at the same time as the main Tanllwyth in February 1996. For the paired sites, both streams and boreholes were monitored fortnightly. In the case of the manipulation site, the monitoring of the stream continued up to 14th February 2001, whilst sampling was curtailed at the control site and the boreholes on the 27th April 1999 due to lack of sufficient funds to maintain them.

All the samples were filtered through 0.45 μm membranes in the field and stored in a combination of 10% acid washed polyethylene bottles, chromic acid washed glass bottles and distilled water washed glass bottles prior to analysis. On return from the field, the samples were stored in the dark at 4°C — in the case of samples for trace element analysis concentrated nitric acid (ARISTAR grade) was added to a 1% v/v to avoid sample deterioration. Samples were initially analysed at the Plynlimon and later at the CEH Bangor laboratories for pH and Gran alkalinity using electrometric techniques described in Neal *et al.*, (1997a). Other determinands were measured at CEH Wallingford using a combination of automated colorimetry, ion chromatography and inductively coupled plasma optical emission and mass spectrometry techniques (Neal *et al.*, 1997a). Within the later part of the dataset, no values are available for several of the trace elements and for bromine. The trace element shortfall results from the loss of the ICPMS facility (from 17th November 1998) while bromine, the loss of the colorimetrically based autoanalyzer methodology (method of Moxon and Dixon, 1980) from 1st December 1999 meant that a new methodology had to be introduced and the data loss was based on ion chromatography. Comparisons of results for the old and new methodologies show marked differences with the new methodology typically showing concentrations half those of the earlier methodology and a yearly cyclical pattern has been lost. It may be that the earlier methodology picked up an organo-bromine signal from the humic acids present in the water: the ion chromatography method specifically determines only bromide.

Results and discussion

The data for the main stem of the Nant Tanllwyth are presented here, followed by a summary for the paired catchment dataset. This separation is needed as the monitoring periods differ in length and quite different features are observed.

THE MAIN STEM OF THE NANT TANLLWYTH

Tables 1a, 2 and 3 summarise the water quality of the main stem of the Nant Tanllwyth: Table 1b shows the equivalent information for rainfall and cloud-water. For these tables, the data are subdivided into three groups: (1) the pre-fell periods (from the start of monitoring until the onset of felling at the end of February 1996, (2) the period of fell, a two year period starting with the onset of felling, and (3) the post-fell period, from two years after the onset of felling and up to the end of the current data record, the end of December 2002. Table 1 gives the average and range (minimum and maximum) concentrations, while Table 2 shows the average baseflow and stormflow concentrations; the averages for the baseflow and stormflow periods cover the lowest 10% and the highest 10%, respectively, of flows for each of the pre-fell, fell and post-fell periods. Table 3 provides a summary of the flow weighted concentrations of the various water quality determinands, an assessment of the total wet deposition and the net uptake or export of chemicals to or from the catchment.

To do this, four steps were involved. Firstly, the flow-weighted average concentration was taken as the sum of the products of the concentration and flow divided by the sum of the flows. In the case of the rainfall and cloud-water components, the 'flow' used for the flow weighting was the volume of catch while for the streams, the flow is the instantaneous flow at the time of sampling. Secondly, the total wet deposition comprises rainfall and cloud-water. However, there is no direct measurement of cloud-water input to the catchment: the collector is designed specifically as an efficient collector of cloud-water rather than a representative aerially averaged volume of catch representative of vegetation surfaces: at times, the cloud-water catch could be over ten times higher than that for rainfall. The catch area for the cloud-water collector depends on the volume of air that passes through the strings, which

Table 1a. A summary of averages and minima and maxima for stream water quality, for the periods pre-fell, at the time of fell (and for the next two years), and the period post two years after fell. All concentrations are as "atomic rather than species weight except for the * terms ammonium (µg-NH4 l^{-1}), sulphate (mg-SO_4 l^{-1}) and nitrate (mg-NO s:$_3$ l^{-1}).

		Pre-Fell			Fell			Post-Fell		
		Average	*Minimum*	*Maximum*	*Average*	*Minimum*	*Maximum*	*Average*	*Minimum*	*Maximum*
Na	mgl^{-1}	4.84	3.22	6.54	4.67	3.65	7.10	4.31	2.42	7.79
K	mgl^{-1}	0.19	0.09	0.40	0.27	0.14	0.64	0.21	0.08	1.00
Mg	mgl^{-1}	0.95	0.35	1.83	1.01	0.63	1.34	0.80	0.29	1.41
Ca	mgl^{-1}	1.48	0.43	4.13	1.60	0.54	2.91	1.19	0.28	2.48
NH_4	$\mu g^{*}l^{-1}$	11	0	160	22	0	1120	16	0	256
Cl	mgl^{-1}	8.3	5.5	14.0	7.8	3.8	16.2	7.2	3.9	18.8
SO_4	$mg^{*}l^{-1}$	5.7	3.8	10.3	5.9	4.0	9.2	4.5	2.5	7.2
NO_3	$mg^{*}l^{-1}$	2.5	0.9	5.3	2.7	0.9	7.1	1.2	0.0	6.8
F	μgl^{-1}	46	0	90	50	30	80	39	0	100
Br	μgl^{-1}	27	18	44	29	20	57	30	21	60
I	μgl^{-1}	1.7	1.0	2.9	1.7	0.9	3.6	2.0	0.9	4.8
PO4	μgl^{-1}	1.4	0	30	18.9	0	550	2.1	0	50
DOC	M	2.58	0.8	8.0	2.77	0.9	12.1	3.65	1.2	16.0
Si	mgl^{-1}	1.57	0.60	2.25	1.73	0.45	2.30	1.50	0.45	2.35
pH		5.29	4.17	6.83	5.41	4.13	6.94	5.21	4.07	6.61
GAlk	μEql^{-1}	-4	-78	237	-2	-92	102	-3	-115	160
Al	μgl^{-1}	339	12.7	836	296.	50.8	789	300	57.6	776
B	μgl^{-1}	5.7	2.5	23.2	5.6	3.2	8.5	6.8	1.2	17.4
Ba	μgl^{-1}	5.5	2.1	26.9	5.9	3.4	10.4	5.9	3.3	16.6
Co	μgl^{-1}	4.7	0.3	8.3	5.2	1.3	8.0	4.5	1.2	9.2
Cu	μgl^{-1}	2.3	0.5	7.9	2.0	0.5	3.4	2.0	0.0	17.2
Fe	μgl^{-1}	215	109	508	247	139	604	298	129	1030
Li	μgl^{-1}	2.8	1.2	4.8	2.7	1.7	3.5	2.5	0.9	5.2
Mn	μgl^{-1}	96.4	37.2	153.8	105.6	44.8	156.4	89.8	21.6	167.4
Ni	μgl^{-1}	3.8	1.1	9.9	3.5	1.0	6.3	NA	NA	NA
Pb	μgl^{-1}	0.9	0	23.5	0.7	0	3.3	NA	NA	NA
Rb	μgl^{-1}	0.4	0.2	1.2	0.5	0.3	1.3	NA	NA	NA
Sr	μgl^{-1}	6.9	3.3	16.0	6.6	3.7	9.3	5.4	1.8	9.0
Y	μgl^{-1}	0.4	0.1	0.8	0.4	0.2	0.7	NA	NA	NA
Zn	μgl^{-1}	17.7	4.1	135.5	24.0	7.6	87.9	27.3	7.2	330.2

is a function of wind speed and the moisture content of that air. Hence, the cloud-water component had to be estimated following Wilkinson *et al.* (1997) who determined that the volume of cloud-water deposition in the upper parts of Plynlimon amounted to 33 mm yr^{-1} for moorland and 140 mm yr^{-1} for forest. Thirdly, because of doubts about the reliability of the rainfall measurements, the water balance is uncertain (Hudson *et al.*, 1997b) to the degree required for chemical flux estimation (Neal and Kirchner, 2000). Further, uncertainties of water residence times for the catchment mean that there may be significant errors for the shorter lengths of data such as those presented in this paper. To calculate the wet deposition input-output balances, the flow weighted concentrations for a total wet deposition estimate have been compared with the stream water on the basis that there is a net balance for the chemically conservative ion chloride. The input-output relationship is estimated for individual components (X) as % loss of the wet deposition input (rainfall and cloud water) by:

$$\% \text{ loss} = 100*(X_{Stream} - (X_{WD}*Cl_{Stream}/Cl_{WD}))/X_{Stream}.$$

Table 1b. A summary of averages and minima and maxima for rainfall and cloud water quality, for the periods pre-fell, at the time of fell (and for the next two years), and the period post two years after fell. All concentrations are as "atomic rather than species weight except for the * terms ammonium (µg-NH_4 l^{-1}), sulphate (mg-$SO_4 l^{-1}$) and nitrate (mg-$NO_3 l^{-1}$).

		Rainfall									Cloud water								
		Pre-Fell			*Fell*			*Post-Fell*			*Pre-Fell*			*Fell*			*Post-Fell*		
Date		*avg*	*min*	*max*	*avg*	*min*	*max*	*avg*	*min*	*max*	*avg*	*min*	*max*	*avg*	*min*	*max*	*avg*	*min*	*max*
Na	mgl^{-1}	1.95	0.1	13.0	1.72	0.1	11.8	2.08	0.1	18.7	42.3	1.6	1034	32.8	1.3	227	29.1	1.1	120
K	mgl^{-1}	0.14	0	1.95	0.14	0	1.54	0.12	0	0.83	1.87	0.1	44	1.64	0.2	13.1	1.47	0.2	7.3
Mg	mgl^{-1}	0.24	0	1.7	0.22	0	1.4	0.29	0	3.1	5.17	0.2	130.5	4.10	0.1	30.9	3.50	0.2	14.9
Ca	mgl^{-1}	0.56	0	11.8	0.46	0.1	3.4	0.45	0	22.6	4.10	0.2	107	4.22	0.2	81	2.29	0.3	18.9
NH_4	mg^*l^{-1}	0.54	0	4.4	0.63	0.1	4.1	0.31	0	1.7	5.62	0.1	54	6.73	0	49	3.33	0	42
Cl	mgl^{-1}	3.7	0.5	23.0	3.2	0.4	24.6	3.6	0.2	34.0	56.1	1.7	740	47.7	2.4	256	48.4	1.5	184
SO_4	mg^*l^{-1}	2.8	0.4	30.0	2.5	0.6	13.6	1.6	0.4	12.4	25.6	0.9	510	23.2	3.8	154	14.0	2.1	9
NO_3	mg^*l^{-1}	1.6	0.2	11.8	1.7	0.0	10.2	0.9	0.1	8.7	21.5	0.5	205	25.6	1.0	160	14.4	0.6	220
F	μgl^{-1}	15.0	0.0	140	25.1	0.0	80	13.8	0.0	60	76.2	0.0	630	73.0	0.0	370	48.9	0.0	470
Br	μgl^{-1}	14.0	3.0	69	12.3	1.0	63	NA	NA	NA	172	6.0	2300	141	20	720	NA	NA	NA
I	μgl^{-1}	1.5	0.4	5.2	1.5	0.5	3.6	1.4	0.6	3.3	10.6	0.8	40	11.4	1.2	50	9.7	1.1	66
PO_4	μgl^{-1}	18.5	0	387	9.4	0	280	NA	NA	NA	96.1	0	1980	119	0	940	39.7	0	820
DOC	mgl^{-1}	0.99	0	4.2	0.84	0	4.1	0.56	0	1.9	2.64	0	16.4	3.33	0.4	23.1	1.78	0.3	15.0
Si	mgl^{-1}	0.03	0	1.3	0.01	0	0.3	0.03	0	4.0	0.08	0	0.95	0.08	0	1.35	0.04	0	1.50
pH		4.82	3.49	6.95	4.90	3.83	6.06	5.10	4.04	6.36	4.61	2.92	6.88	4.69	0.00	7.00	4.91	3.04	6.99
GAlk	μEql^{-1}	-30	-324	26	-20	-100	12	-9	-73	96	-112	-1202	105	-65	-783	734	-29	-800	132
Al	μgl^{-1}	19.9	0	320	12.9	1.2	170	11.6	0	72	152.5	0	5892	99.7	4.1	1345	60.7	0	842
B	μgl^{-1}	5.6	0	99.4	2.8	0	8.2	NA	NA	NA	129.7	0.0	4930.0	16.1	3.3	70.4	15.2	1.2	75.7
Ba	μgl^{-1}	6.2	0.2	194	1.6	0.3	14.0	4.3	0	102	13.3	0.6	299	11.0	1.8	113	9.5	0.8	67
Co	μgl^{-1}	0.1	0	2.8	0.1	0.0	0.6	0.2	0	15.3	0.4	0	15.7	0.5	0.0	6.7	0.4	0	4.9
Cu	μgl^{-1}	2.5	0.1	47.7	1.2	0.3	5.8	0.9	0	21.5	12.6	0.2	427	10.4	0.4	138	13.7	0	202
Fe	μgl^{-1}	16.0	0	374.	24.6	0	976	12.9	0	136	100.9	0.0	2332	101.3	4.3	681	55.3	1.6	1004
Li	μgl^{-1}	0.1	0	2.2	0.0	0	0.3	0.0	0	1.0	1.4	0.0	64.8	0.8	0.0	6.9	0.7	0	4.4
Mn	μgl^{-1}	2.7	0	58.3	2.6	0	35.1	1.6	0	22.7	30.2	0.0	1130	36.2	0.3	943	14.1	0.6	221
Ni	μgl^{-1}	0.9	0	18.0	0.5	0	5.8	1.2	0	107	5.6	0	235	3.2	0	27.5	NA	NA	NA
Pb	μgl^{-1}	89.1	0.4	2936	31.8	1.6	295	NA	NA	NA	48.6	0.3	3384	24.9	0.4	198	NA	NA	NA
Rb	μgl^{-1}	0.2	0	1.8	0.1	0.0	0.7	NA	NA	NA	1.8	0.1	114	1.3	0.2	14.6	NA	NA	NA
Sr	μgl^{-1}	2.6	0.3	23.7	2.0	0.4	10.5	2.3	0.3	85	47.5	1.0	2506	27.8	1.7	233	23.1	1.7	127
Zn	μgl^{-1}	19.1	0.7	170	11.6	1.6	78	13.5	0	143	128.0	2.2	7156	136.2	9.7	2695	87.9	12.5	567

For this equation the subscripts 'Stream' and 'WD' refer to the stream and wet deposition, respectively, while 'Cl' refers to chloride. Finally, it must be appreciated that the estimates are only an approximation. Indeed, much more detailed measurements of cloud-water deposition, spatial coverage and chemistry of rainfall and stream responses to storm events would be required to determine the actual flux changes. In the present case, the estimated evapotranspiration based on the chloride concentrations in total wet deposition and in the stream amounts to about 47, 10 and 35% of the input, for the pre-fell, fell and post-fell periods, while the corresponding volumetric estimates (based on hydrological measurements of flow, coupled with the cloud-water deposition estimates of Wilkinson *et al.* (1997) are 16, 23 and 19%: the longer term average for moorland and forest based on hydrological data at Plynlimon is 20 and 25% for moorland and forest, respectively: Neal and Kirchner, 2000). The higher evapotranspiration estimates based on chloride measurements could reflect either from an overestimation of the cloud-water component (the Tanllwyth catchment is at lower altitude than the top of the Severn where Wilkinson *et al.* 1997, made their estimates of volumetric deposition) or some high chloride events in the stream have been missed (with relatively low permeable soils, the Nant Tanllwyth has hydrologically a particularly 'flashy' catchment) and thus prone to such errors.

The tables contain no data for the trace elements Be, Cd, Ce, Cr, Cs, La, Mo, Pr, Sb, Sc, Th, U or the lanthanides because the concentrations were all less than 0.5µg l^{-1}; these concentrations are at or below the detection limits for the methods of analysis used.

The salient features of the results are as follows.

Table 2. A summary of baseflow and stormflow chemistries for the Nant Tanllwyth, for the periods pre-fell, at the time of fell (and for the next two years), and the period post two years after fell. All concentrations are as "atomic rather than species weight except for the * terms ammonium (µg-NH_4 l^{-1}), sulphate (mg-SO_4 l^{-1}) and nitrate (mg-NO_3 l^{-1}).

		Pre-Fell		Fell		Post-Fell	
		Baseflow	*Stormflow*	*Baseflow*	*Stormflow*	*Baseflow*	*Stormflow*
Na	$Mg1^{-1}$	5.16	4.41	4.79	4.47	4.58	4.09
K	mgl^{-1}	0.20	0.20	0.26	0.36	0.18	0.27
Mg	mgl^{-1}	1.15	0.72	1.18	0.83	0.94	0.63
Ca	mg^{l-1}	2.34	0.75	2.44	0.83	1.82	0.69
NH_4	$\mu g^{*}l^{-1}$	8.29	9.52	11.09	124.73	14.95	35.71
Cl	mgl^{-1}	8.8	8.0	7.5	7.7	7.2	7.5
SO_4	$mg^{*}l^{-1}$	6.0	5.2	6.2	5.7	5.1	3.8
NO_3	$mg^{*}l^{-1}$	1.8	2.3	1.9	3.5	0.7	1.5
F	μgl^{-1}	47	47	46	53	37	39
Br	μgl^{-1}	27	32	28	36	24	41
I	μgl^{-1}	1.8	1.9	1.9	1.7	2.3	1.8
PO_4	μgl^{-1}	2.4	1.4	12.7	68.2	1.0	9.5
DOC	mgl^{-1}	1.88	4.57	1.82	5.56	2.45	4.77
Si	mgl^{-1}	1.95	0.95	2.01	1.10	1.84	0.95
pH		6.46	4.37	6.65	4.31	6.21	4.50
G Alk	μEql^{-1}	44	-53	60	-62	37	-42
Al	μgl^{-1}	85.3	545	75.4	632	108	463
B	μgl^{-1}	6.8	5.6	6.0	5.7	8.4	7.1
Ba	μgl^{-1}	5.4	5.3	4.2	6.4	5.9	6.2
Co	μgl^{-1}	3.8	3.7	2.8	5.43.2	4.0	
Cu	μgl^{-1}	1.9	2.9	1.5	2.7	1.5	2.8
Fe	μgl^{-1}	212	243	262	273	283	264
Li	μgl^{-1}	3.0	2.0	2.9	2.2	3.1	1.8
Mn	μgl^{-1}	114.8	58.4	95.3	71.4	94.5	60.2
Ni	μgl^{-1}	3.1	3.9	2.8	3.8	NA	NA
Pb	μgl^{-1}	1.3	1.5	0.3	1.7	NA	NA
Rb	μgl^{-1}	0.4	0.4	0.5	0.7	NA	NA
Sr	μgl^{-1}	8.4	5.0	7.6	5.3	6.8	4.1
Y	μgl^{-1}	0.2	0.5	0.2	0.6	NA	NA
Zn	μgl^{-1}	12.3	16.9	23.9	27.0	21.0	50.4

Rain water, cloud-water and stream water chemistries are relatively dilute, but there are large ranges in concentration for most chemical determinands. Rainfall is usually the most dilute of these waters and cloud-water is the most concentrated. Further, rainfall and cloud-waters are more acidic (lower pH and lower Gran alkalinity) than the stream. This corresponds to the well established relationships between wet deposition inputs and stream chemistry where the variability in atmospheric inputs for the relatively inert chemicals are damped out within the catchment (this is particularly so for the 'sea salt' components Na and Cl) and partial neutralisation of the acidic input occurs due to weathering reactions within the catchment. The most concentrated rainfall and cloud-waters occur for small

Table 3. A summary of rainfall, cloud water, total wet deposition and stream water flow weighted concentrations and catchment losses, for pre-fell, fell and post-fell periods. All concentrations are as "atomic rather than species weight except for the * terms ammonium (µg-NH_4 l^{-1}), sulphate (mg-SO_4 l^{-1}) and nitrate (mg-NO_3 l^{-1}).

		Rainfall			Cloud			Total Wet Dep			Stream			% loss		
		Pre-Fell	*Fell Fell*	*Post-*	*Pre-Fell*	*Fell Fell*	*Post-*	*Pre-Fell*	*Fell Fell*	*Post-*	*Pre-Fell*	*Fell*	*Post-Fell*	*Pre-Fell*	*Fell*	*Post-Fell*
Na	mgl^{-1}	2.14	2.26	2.41	26.74	25.75	24.67	3.29	3.66	3.29	4.84	4.48	4.22	1	12	-9
K	mgl^{-1}	0.11	0.11	0.12	1.11	1.10	1.20	0.15	0.17	0.16	0.22	0.33	0.28	-5	82	34
Mg	mgl^{-1}	0.25	0.27	0.31	3.14	3.08	2.94	0.38	0.44	0.42	0.87	0.87	0.70	81	88	31
Ca	mgl^{-1}	0.25	0.26	0.33	1.87	1.92	1.57	0.33	0.36	0.39	1.02	1.07	0.82	165	186	76
NH_4	mg^*l^{-1}	0.31	0.37	0.21	3.36	3.28	1.84	0.45	0.55	0.28	0.01	0.17	0.03	-143	-79	-125
Cl	mgl^{-1}	4.1	4.3	4.1	45.8	43.9	42.7	6.0	6.7	5.7	8.8	7.4	7.7	0	0	0
SO_4	mg^*l^{-1}	1.6	1.6	1.3	14.3	12.9	10.2	2.2	2.3	1.7	5.5	5.9	4.0	107	144	102
NO_3	mg^*l^{-1}	0.8	1.0	0.6	11.3	11.5	7.1	1.3	1.6	0.8	2.7	3.5	1.5	60	110	43
F	mgl^{-1}	0	0	0	0	0	0	0	0	0	0	0.1	0	248	127	196
Br	μgl^{-1}	15.6	15.1	NA	142.2	132.8	NA	21.5	22.2	NA	30.4	35.0	NA	-5	48	NA
I	μgl^{-1}	1.2	1.2	1.2	8.6	9.3	7.7	1.6	1.7	1.5	1.8	1.8	1.8	-36	-5	-16
PO_4	μgl^{-1}	16.0	9.0	NA	37.0	45.0	19.0	17.0	11.3	NA	1.0	93.0	11.0	-140	716	NA
DOC	mgl^{-1}	0.69	0.60	0.42	1.68	1.78	1.16	0.74	0.69	0.45	3.44	5.16	4.53	321	643	862
Si	mgl^{-1}	0.05	0.01	0.03	0.08	0.06	0.02	0.05	0.02	0.03	1.20	1.26	1.05	2230	8038	2891
pH		5.00	5.04	5.19	4.97	5.00	5.09	5.00	5.15	5.26	4.63	4.63	4.65	na	na	Na
GAlk	μEql^{-1}	-14	-13	-3	-47	-3	-12	-16	-13	-3	-37	-44	-34	85	230	934
Al	μgl^{-1}	6.2	5.7	10.5	48.1	35.4	34.5	8.2	7.6	11.6	536.7	522.0	417.6	6427	6797	3469
B	μgl^{-1}	3.0	2.5	NA	88.3	11.8	12.2	7.0	3.1	NA	5.4	5.4	7.1	-69	66	NA
Ba	μgl^{-1}	1.6	0.9	2.8	5.4	5.6	6.2	1.8	1.2	3.0	5.7	6.2	7.2	166	393	105
Co	μgl^{-1}	0.0	0.0	0.2	0.2	0.2	0.3	0.0	0.0	0.2	4.3	5.4	4.2	8417	10782	2082
Cu	μgl^{-1}	1.5	0.7	0.8	5.4	3.8	6.7	1.7	0.9	1.0	2.8	2.5	2.4	17	159	96
Fe	μgl^{-1}	5.0	7.5	10.9	40.0	42.1	30.6	6.7	9.6	11.8	215.2	255.5	287.8	3087	2538	2302
Li	μgl^{-1}	0.1	0.0	0.0	0.6	0.5	0.6	0.1	0.1	0.1	2.4	2.3	2.0	2376	3395	3691
Mn	μgl^{-1}	0.9	1.0	1.1	9.7	10.9	6.9	1.3	1.6	1.3	74.6	83.6	70.7	5600	5141	5312
Ni	μgl^{-1}	0.5	0.2	NA	2.3	1.4	2.0	0.5	0.3	1.2	3.9	3.7	NA	581	1129	NA
Pb	μgl^{-1}	30.4	15.2	NA	13.2	8.8	NA	29.6	15.2	NA	1.2	1.5	NA	-142	-100	NA
Rb	μgl^{-1}	0.1	0.1	NA	0.7	0.7	NA	0.1	0.1	NA	0.4	0.6	NA	258	446	NA
Sr	μgl^{-1}	2.0	1.9	2.2	21.7	20.0	18.7	2.9	3.0	2.9	5.9	5.7	4.6	59	80	23
Y	μgl^{-1}	0.0	0.0	NA	0.1	0.0	NA	0.0	0.0	NA	0.5	0.5	NA	4600	8246	NA
Zn	μgl^{-1}	8.1	6.5	10.7	57.6	62.7	61.0	10.4	9.8	12.7	19.4	28.6	38.9	41	182	169

volumes of catch and this corresponds with a 'washout' of particulates during events, where higher volumes of water lead to greater dilution. Within the streams, there is a marked variation in water quality linked to contrasting baseflow and storm water conditions. Under baseflow conditions, the waters are of relatively low acidity (pH typically around 6.5) and of positive Gran Alkalinity (around 40 µEq l^{-1}). The baseflow waters are Ca and Mg bearing with concentrations around 1.1 and 2.4 mg l^{-1}, respectively, and they are enriched in silicon (typically around 1.8 mg-Si l^{-1}). In contrast, storm flow waters are highly acidic (pH typically around 4.3) of negative Gran alkalinity (typically around –50 µEq l^{-1}) and they are enriched in aluminium (typically 500 µg l^{-1}) and dissolved organic carbon (DOC, typically around 5 mg-C l^{-1}), but they are depleted in base cations and silicon. These differences simply reflect the changing dominance of stream inputs from two distinct hydrogeochemical zones. Under storm flow conditions, the

waters are derived mainly from the soil zone where acidic conditions prevail. Within the soil zone, aluminium is available for acid leaching from oxide and hydroxides which are present in the soil matrix, while the soil waters are organic-rich from humic and fulvic acids generated from the organic components in the soil matrix. Under baseflow conditions, the waters are from the lower soils and shallow groundwater zones where weathering reactions ensure that the soil waters lose much of their acidity and convert dissolved carbon dioxide into bicarbonate anions while releasing divalent base cations from carbonate and silicate phases and silicon from the silicate phases. In the process, aluminium is precipitated from solution due to hydrolysis under less acidic conditions while DOC is lost as carbon dioxide/bicarbonate. These patterns are observed prior to, during and post-felling.

Wet deposition inputs and stream output chemistries have to be considered in relation to pre-felling, felling and post-felling times.

Prior to felling, there is an approximate balance for sodium and potassium (and chloride by definition), but for most other components there is a marked imbalance. This imbalance takes two forms.

Firstly, some components are enriched in runoff. These components divide into three distinct hydrogeochemically reactive types:

- **The divalent base cations, Gran Alkalinity, fluoride and silicon** (80 to over 2000% enrichment). The divalent base cations (Mg, Ca, Sr and Ba: 59 to 166% enrichment) are in part derived from weathering of the bedrock as described earlier. Within this group is fluoride (248% enrichment) which is strongly associated with aluminium within the soil and groundwater matrix, while silicon is derived mostly from the weathering of silicates within the bedrock (2230% enrichment).
- **Sulphate and nitrate** (60 to 107% enrichment). These components are essentially derived from the atmosphere, but not simply in the form of wet deposition. An important part of the deposition comes from uptake of gaseous inputs to the vegetation surface (SO_x and NO_x: RGAR, 1997).
- **Many trace metals** (40 to over 8000% enrichment). These trace metals (Al, Co, Fe, Li, Mn, Ni, Rb, Y, Zn) are mainly mobilised under acidic conditions where hydrolysis is minimal and where organic rich solutions can enhance solubility due to complexation reactions.

Secondly, there are components where the atmospheric inputs are retained by the catchment and there is insufficient release by the catchment to allow even a net balance. There are three hydrogeochemically distinct types:

- **Bromine and iodine** (5 to 36% loss). These components are derived mainly from the atmosphere and they originate in the sea. They are nutrients; they take part in biological reactions and they are in part retained by the organic biomass.
- **Ammonium, phosphate and boron** (70 to 143% losses). These components are important nutrients and they fertilise the catchments. In addition, ammonium can be converted to nitrate and it is also taken up onto cation exchange sites in the soil, while phosphate can be precipitated into or sorbed onto iron rich phases which are common within the highly reducing gley soils. Boron is mainly present as borate anions which are of low chemical reactivity and boron shows the lowest uptake within this group.
- **Lead** (about 142% loss). There is an unusually high deposition of lead into the catchment (highest concentrations occur under low volumes of catch in rainfall and it is derived from pollutant emissions to the atmosphere). Within the catchment, lead can sorb onto the organic soils. However, lead also occurs within the bedrock of the area but it seems that, under the less acidic conditions that occur within these areas, the lead is retained in an insoluble form.

With felling, there are initially some moderate increases in concentration for many of the components with a subsequent reduction towards or below pre-fell levels. The changes in water quality with felling are summarised in Tables 1 and 2 and illustrated as time series in Figs. 1a and 1b for Na, K, SO_4, Fe, NO_3 and Gran alkalinity. In Fig. 1a, the time series plots are for the Nant Tanllwyth, while the plots in Fig. 1b are for the Afon Hafren which is used as a marker to set against the changes observed in the Nant Tanllwyth. Note that the Hafren has been felled progressively through the years but there is little effect on stream water quality (other than perhaps for potassium concentrations) as the phased felling results in runoff from different parts of the catchment that are influenced by the early felling effects as well as the recovery phase (Neal *et al.*, 2003a). The patterns of change observed are as follows.

- **Sodium and chloride**. These components are largely derived from the atmosphere. Through the felling and post-felling period, the concentrations fall moderately (about 10%) without a corresponding fall for the Hafren control. This feature would be expected due to reduced scavenging of cloud-water inputs which are enriched in sea-salt components and increased runoff due to reduced

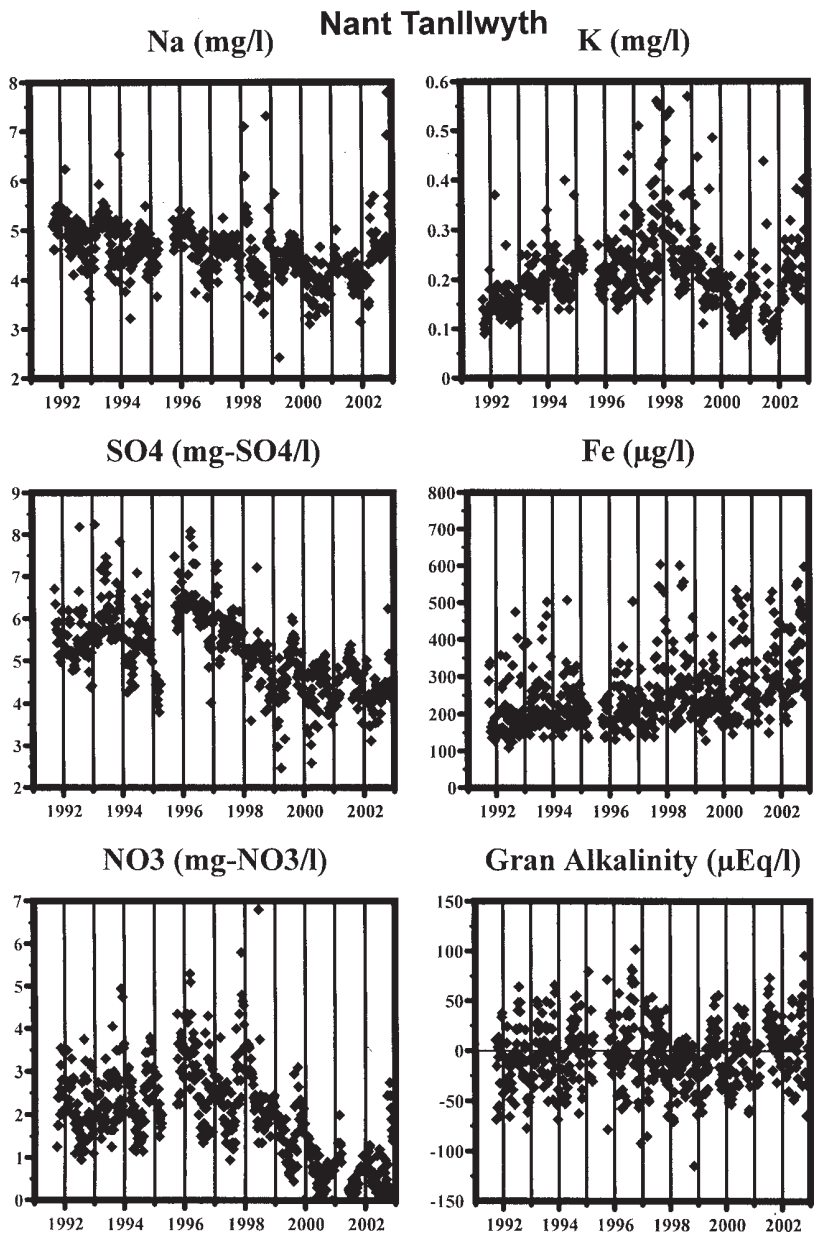

Fig. 1a. *Time series data for Na, K, SO_4, Fe, NO_3 and Gran alkalinity for the main stem of the Nant Tanllwyth.*

transpiration as trees are removed from the catchment.

- **Ammonium, potassium, and phosphate**. Initially, these increase with felling and subsequently fall towards pre-fell values. These components are taken up in the growing biomass, and the loss of tree cover ensures minimal uptake at a time when releases from decomposing fine roots, needles etc are increasing. On a proportionate basis, the increase in phosphate is the greatest (an order of magnitude change), but other than an exceptionally high spike at 550 µg-P l^{-1} observed within the first two years of fell concentrations are still low throughout the period. For ammonium, concentrations on average double initially on felling, but again there is a very high spike observed during this period (1120 µg-NH_4 l^{-1}). These changes have not been observed within the Hafren.
- **Nitrate**. Usually, nitrate shows a major increase with felling due to the disruption of the nitrogen cycle. However, in this case, other than a decrease in concentration post-felling there is no clear change. Such a change is not observed for the Hafren and it seems that felling has led to uptake rather than release.
- **Sulphate**. There is a clear decline in sulphate concentration following felling. However, in the Hafren

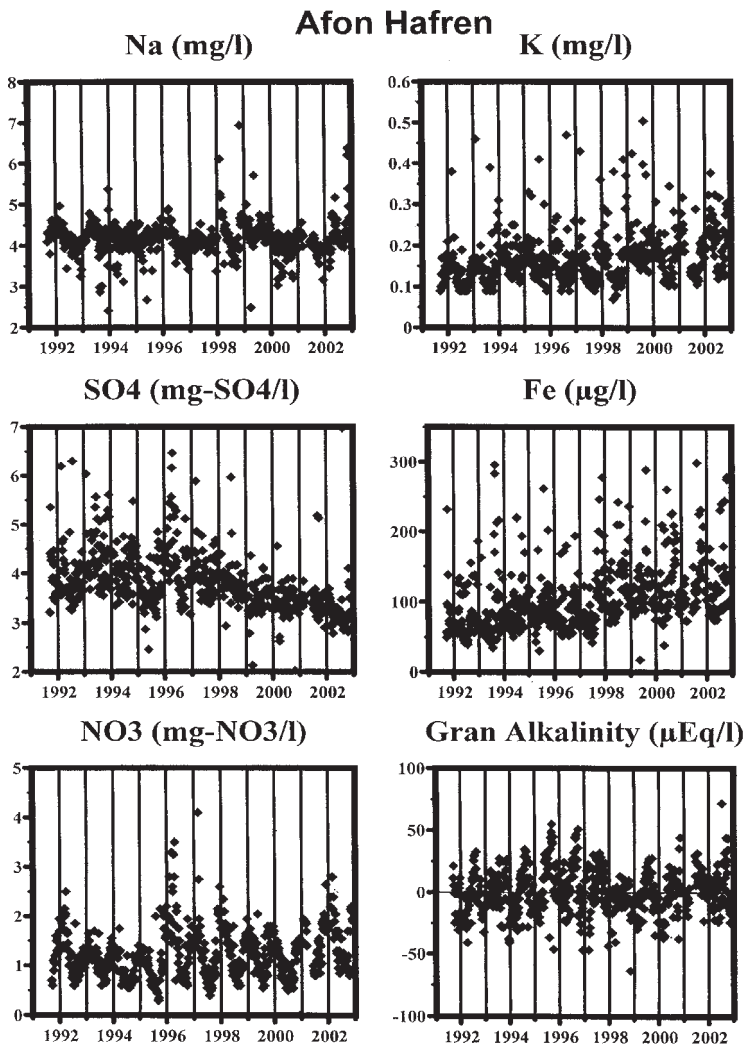

Fig. 1b. *Time series data for Na, K, SO_4, Fe, NO_3 and Gran alkalinity for the main stem of the Afon Hafren at its lowest gauging point.*

there is a similar decline and the reduction may well be linked to factors other than felling such as declining atmospheric deposition and attenuation in the soil associated with sorption-desorption processes (Neal *et al.*, 2001).

- **Iron and DOC**. These components increase through the study period as is observed across all the forested Plynlimon catchments and it is not associated with felling (Neal *et al.*, 2001: also see Fig. 1b in this paper for the Hafren).
- **Other components.** For all other components there is little change.

The effects of borehole introduction on stream water chemistry

While not central to this paper, it is appropriate to show the effect of the deep borehole introduction near the main stem on the stream pH and Gran alkalinity. This borehole not only opened a groundwater route to the stream, but also allowed the transfer of both base-rich high alkalinity waters and, occasionally, acidic soil waters to the stream (Neal *et al.*, 1997b). This section illustrates how the water quality has changed since and initial report by Neal *et al.* (1997b) to describe the longevity in the improvement of water quality due to the groundwater introduction. This aspect is important in relation to practical environmental management to reduce stream acidification. Here, it is sufficient to concentrate solely on pH and Gran alkalinity changes, which have been monitored at both the upstream and downstream sites (unlike the major ion chemistry which was discontinued at the lower site when the upstream site was introduced).

Figure 2 shows the salient features where pH (left-hand side of Fig. 2) and Gran alkalinity (right-hand side of Fig. 2) is plotted as (a) a time series for the downstream location

influenced by the borehole (the top row of diagrams) which covers the full length of record, (b) the time series difference for the upstream and downstream data record (the middle row of diagrams) to show the scale of change and (c) the change in pH and Gran Alkalinity relative to the downstream values (the bottom row of diagrams). The salient features are as follows.

- Following the borehole introduction, the pH increased by over 0.5 units under baseflow conditions when the pH is at its highest. The increase in Gran alkalinity is much more marked than for pH and can be as high as 530 μEq l^{-1}.
- There is a large scatter to the data. This is due to the influence of flow. Under baseflow conditions, the pH at its highest and the influence of the borehole is maximal. Under stormflow conditions, the pH is low due to the input of acidic soil water which dilutes the groundwater input.
- The maximum change in pH occurs at intermediate values of pH (up to about 1 unit of change) but for Gran alkalinity, there is a progressive and accelerating change to higher Gran alkalinity values.
- The influence of the borehole may recede with time (as shown by decreasing maximum determinand changes over time), but the reduction is relatively small as that the influence of the borehole remains after six years.

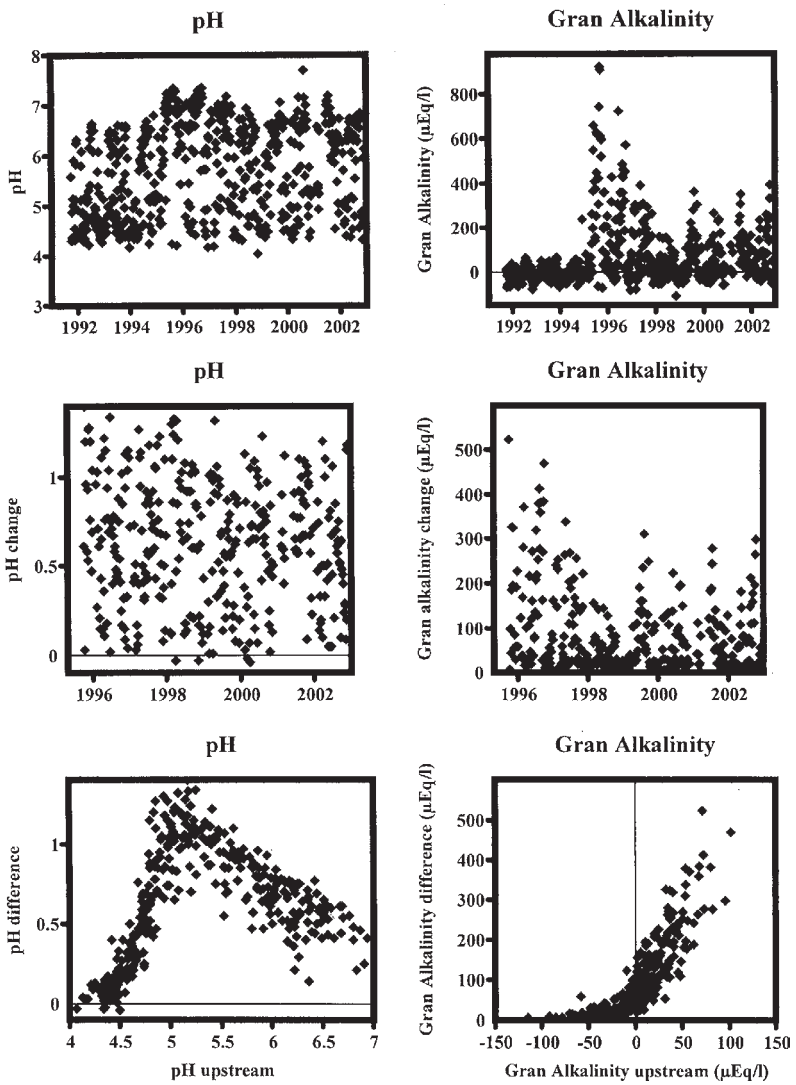

Fig. 2. *Plots are presented illustrating the effects of groundwater inputs to the Nant Tanllwyth due to the introduction of a borehole by the side of the stream on a nearby bank. The figures are for pH (left hand side of the figure) and Gran alkalinity (right hand side of the figure). The top row of graphs show time series for the downstream location influenced by the borehole and the time series covers the full monitoring period from 1991 to 2003. The middle row of graphs shows time series for the difference in pH and in Gran alkalinity for upstream and downstream data record and this shows the scale and longevity of change. Note that in this case, the plot covers only the period post borehole introduction (1995 to 2003). The lower set of graphs shows change in pH and Gran Alkalinity relative to the downstream values.*

THE PAIRED CATCHMENTS

Stream chemistry

The water quality changes for the control and manipulation sites are provided in Table 4 where the data for the manipulation site is subdivided into pre-fell, fell and post-fell periods in the same way as for the main stream. For the control site, the data are restricted to the pre-fell and felling periods due to lack of data for the post-fell period. Time series for selected determinands are provided in Fig. 3 to show the temporal patterns of change for the control site (open circles) and the manipulation site (black filled circles). The salient features are as follows.

- For both the control and manipulation sites, the waters are generally very acidic as they are derived primarily from the low permeability highly acidic soils and they

Table 4. A summary of averages and ranges in water quality for control and manipulation stream sites. For the control, the times corresponding to pre-fell and fell times have been distinguished. For the manipulation site, the pre-fell, fell and post-fell periods are presented. In the case of the control, post fell values are not presented as the data record is insufficient. For the manipulation site, the fell period represents a two year period starting with the commencement of fell. All concentrations are as "atomic rather than species weight except for the * terms ammonium (µg-NH_4 l^{-1}), sulphate (mg-SO_4 l^{-1}) and nitrate (mg-NO_3 l^{-1}).

		Control						Manipulation								
		Pre-fell			*Fell*			*Pre-fell*			*Fell*			*Post-fell*		
		avg	*min*	*max*	*avg*	*min*	*max*	*avg*	*Min*	*max*	*avg*	*min*	*max*	*avg*	*min*	*max*
Na	mgl^{-1}	4.71	3.12	9.04	4.73	2.50	12.43	5.15	3.59	8.93	3.67	2.27	5.86	2.95	1.63	6.22
K	mgl^{-1}	0.07	0	0.51	0.04	0	0.26	0.08	0	0.44	1.93	0.20	3.36	0.55	0.11	1.20
Ca	mgl^{-1}	0.40	0.20	1.04	0.31	0	0.92	0.27	0.09	0.70	0.36	0.13	1.06	0.41	0.07	1.10
Mg	mgl^{-1}	0.71	0.37	1.61	0.66	0.14	2.47	0.61	0.28	1.18	0.67	0.28	0.98	0.58	0.20	1.57
NH_4	$\mu g^{*}l^{-1}$	21	4	78	32	6	162	19	0	98	181	4	850	36	10	330
Cl	mgl^{-1}	7.54	3.5	13.6	8.45	3.6	35.0	8.59	5.1	15.0	6.17	3.3	10.0	4.84	1.3	20.0
SO_4	$mg^{*}l^{-1}$	5.50	2.18	16.31	4.30	1.48	10.22	5.80	2.92	12.07	4.61	1.69	9.91	2.56	1.12	6.61
NO_3	$mg^{*}l^{-1}$	0.13	0	5.3	0.02	0	0.5	0.67	0	5	4.04	0	11	1.97	0.3	11.1
F	μgl^{-1}	29	0	70	39	0	80	36	0	60	42	20	70	22	0	70
Br	μgl^{-1}	69	40	104	67	9	148	40	15	69	84	18	174	42	8	142
I	μgl^{-1}	3.4	1.0	6.6	3.6	0.9	7.2	2.3	0.9	3.9	5.0	1.0	14.1	4.9	1.1	10.5
PO_4	μgl^{-1}	29	0	120	55	0	160	4	0	20	162	0	380	89	0	260
DOC	mgl^{-1}	14.9	5.8	26.4	15.5	4.6	30.6	7.2	1.7	14.4	14.0	2.2	28.8	15.5	5.5	31.5
Si	mgl^{-1}	0.74	0	1.95	0.75	0.15	1.85	0.79	0	1.35	0.80	0.20	1.15	0.54	0	1.35
pH		4.06	3.75	6.06	3.96	3.63	4.48	4.16	3.85	4.80	4.09	3.92	4.42	4.17	3.84	4.33
GAlk	μEql^{-1}	-115	-202	17	-138	-260	-43	-87	-168	-19	-100	-134	-44	-89	-168	-55
Al	μgl^{-1}	426	162	927	439	126	817	529	211	908	717	228	1225	566	133	831
B	μgl^{-1}	6.3	3.1	15.7	5.1	0	11.7	6.7	3.6	26.5	8.8	5.4	16.0	8.0	4.6	22.0
Ba	μgl^{-1}	2.7	0.7	13.3	3.9	1.3	13.7	8.1	2.0	165.0	10.2	3.3	15.2	6.5	2.9	25.9
Co	μgl^{-1}	1.2	0.6	2.8	1.3	0.2	2.9	0.6	0.2	2.9	0.9	0.2	3.1	0.4	0.3	0.6
Cu	μgl^{-1}	2.8	1.4	6.1	4.3	0.8	45.2	2.4	1.3	4.8	5.5	1.5	50.9	3.8	1.4	29.6
Fe	μgl^{-1}	861	216	469	948	162	3210	729	240	1944	941	258	2462	980	57	2326
Li	μgl^{-1}	2.4	0.9	12.9	2.1	0.3	4.9	1.6	0.8	3.3	1.6	0.4	2.7	1.2	0.2	3.3
Mn	μgl^{-1}	19.8	7.9	78.9	13.2	1.5	40.5	10.3	2.1	37.8	13.6	1.8	37.6	12.5	5.1	67.7
Ni	μgl^{-1}	6.0	2.0	25.4	5.8	1.5	15.7	5.0	2.3	10.7	5.6	2.1	12.1	NA	NA	NA
Pb	μgl^{-1}	3.0	1.4	4.7	3.6	1.0	11.2	2.1	0.9	3.5	3.8	1.4	6.8	NA	NA	NA
Rb	μgl^{-1}	0.2	0.0	1.7	0.1	0.0	0.5	0.2	0.1	1.2	2.9	0.3	6.6	NA	NA	NA
Sr	μgl^{-1}	3.3	1.8	6.6	3.0	1.0	9.9	2.2	1.3	4.1	2.8	1.2	5.0	3.0	1.3	8.5
Y	μgl^{-1}	0.2	0.1	0.4	0.2	0.1	0.4	0.1	0.1	0.2	0.3	0.2	0.9	0.3	0.1	0.4
Zn	μgl^{-1}	20.1	9.0	75.9	25.7	9.9	60.6	21.9	7.6	87.7	31.9	12.3	150.8	31.5	10.6	393.8

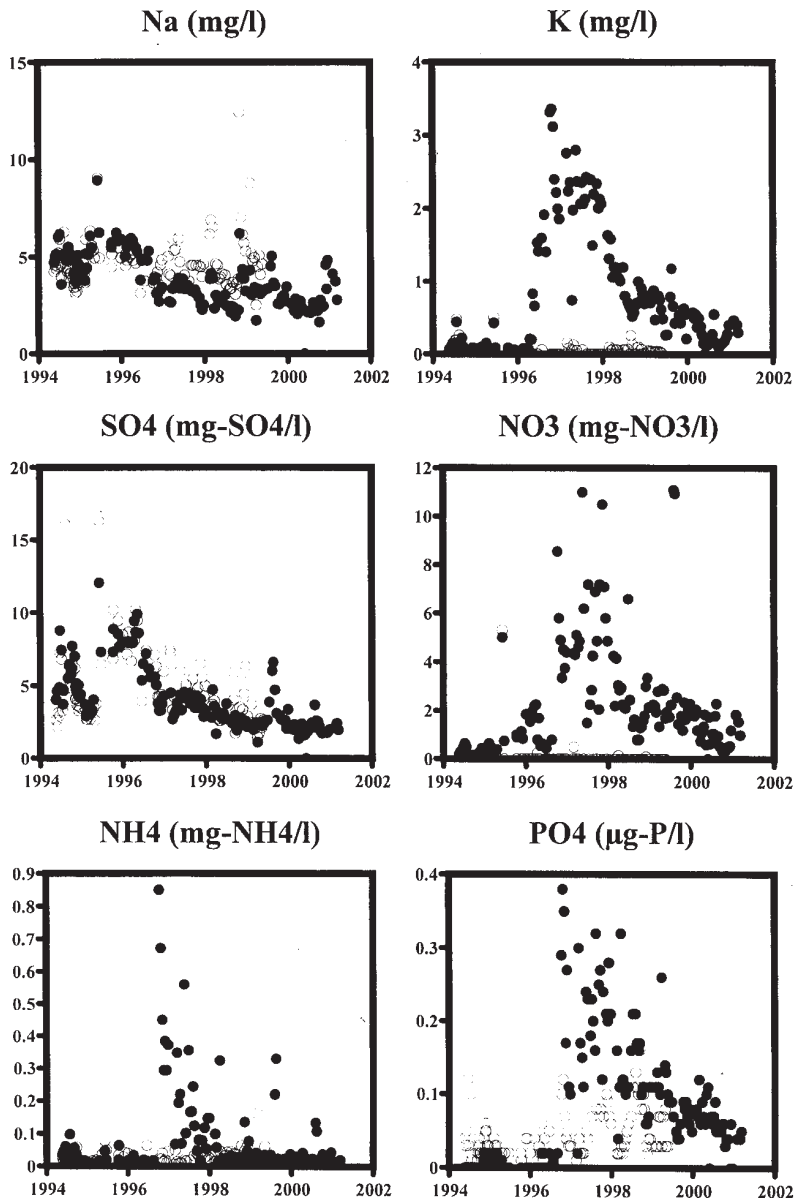

Fig. 3. *Time series plots for Na, K, SO_4, NO_3, NH_4 and PO_4 concentrations at the control (open circles) and manipulation (filled circles) sites. The monitoring of the streams was from 28th April 1994 to 14th February 2001 at the manipulation site while for the control, the monitoring was ended earlier on the 27th April 1999 due to lack of sufficient funds to maintain it.*

have little groundwater component to significantly neutralise the acidity: pH and Gran alkalinity are typically about 4.1 and –100 µEq l^{-1}, respectively. However, for the control, occasionally less acidic waters occur at very low flows in the summer months when biological activity is extremely high. These less acidic waters are generated by the biological loss of nitrate from the stream with no change other than in the pH and the Gran Alkalinity.

- There seems to be no clear effect of felling on the pH and Gran alkalinity: while there are some differences in the averages for the pre-fell, fell and post-fell periods, the high scatter to the data means that any differences in average are not significant statistically.
- With felling there is a lowering in Na and Cl concentrations, as occurred in the main stem of the Nant Tanllwyth: there is no clear change for the control site and no statistically significant trend. The decrease is much greater than for the main stem at around 40%.
- With felling there is also a clear decrease in sulphate, at around the same level as the Na and Cl. However, in this case, the control also shows a similar lowering and it is not clear that felling is having an effect in this case.
- Ammonium, potassium and phosphate all show very

marked increases in concentration with felling followed by a subsequent recovery. This feature, as described for the main stream is a result of the disruption of the biogeochemical cycle with felling. However, in this case, the increase for nitrate is not observed in the main stem of the Nant Tanllwyth: this feature will be discussed later.

- Bromine and iodine. Both these components show moderate increases (a factor of around 2) and subsequent declines with felling. These components are nutrients, and their behaviour would be expected to be similar to that for the other nutrients.
- For the components which show clear changes with felling, the effects are of greater amplitude than for the main stream, where greater dilution occurs.

Groundwater chemistry

The groundwater chemistry at the control and manipulation sites is distinct (Table 5). For example, the control sites are moderately acidic having pH in the range 4.28 to 5.3 with a corresponding Gran alkalinity range of –109 to 89 μEq l^{-1}. In contrast, the manipulation site has a pH in the range of 5.12 to 6.33, while the corresponding range in Gran alkalinity is 25 to 2293 μEq l^{-1}. These contrasting acidities link to the extent of interaction between the soil waters entering the groundwater domain and the extent of weathering therein which neutralises, in part, this incoming acidity. Clearly, the control site represents a situation where the extent of weathering is much lower than the manipulation site as illustrated not only by the differing acidity, but also by the much lower Ca and Mg concentrations; which are generated during the weathering process. Note that there is nonetheless considerable weathering within the groundwater zone, as the stream runoff chemistry is much more acidic than the corresponding groundwater chemistry: the pH range for the streams to set against the values presented above for the groundwaters is 3.63 to 6.06 (remembering that the high values are exceptional due to biological activity), while the corresponding Gran alkalinity range is –260 to 17 μEq l^{-1}).

The groundwater water quality of the control and manipulation sites differs not only in terms of the acidity and degree of weathering, but also in terms of iron and nitrate levels. For the manipulation site conditions must be very reducing because of nitrate levels of almost zero and massively high iron concentrations of up to almost 17 mg l^{-1}. On this basis, the control cannot be compared directly with the manipulation site due to the very distinct chemistry. Rather, the results show the very varied nature of the groundwater system, a feature described previously for the Plynlimon area (Neal *et al.*, 1997c) which often affects the water quality variation in the streams across the landscape (Hill and Neal, 1997; Neal *et al.*, 1997d).

For the manipulation site, describing the effects of felling is difficult as there are major issues of representativeness. During the early part of the monitoring phase, the introduction of the deep borehole near the Nant Tanllwyth affected the chemistry of the main stem. When this borehole to the south of the river was introduced, there was a sudden fall in groundwater level at the manipulation site (early November 1994) even though the two boreholes are on opposite sides of the river. This means that as the borehole allowed transfer of groundwater to the stream it also opened a fracture or a series of fractures which extended below the river and affected the shallow groundwaters to the north of the river. For the manipulation site, the groundwater level changed from about 1 m to about 4 m below the surface. Two weeks after the sudden change in depth at the manipulation borehole, the water quality changed suddenly. This is illustrated in Table 5 where water quality data for the 'early' part of the record, prior to the deep borehole effect, and in the pre-fell period, post the deep borehole effect, are presented. The results show that Ca, Mg, Gran alkalinity, Fe, Ni, Sr and Ba concentrations approximately halved while aluminium concentrations increased. Hence more acidic soil waters entered the system, presumably from the soil and there was a dilution of components generated within the weathering process as well as of iron (released to solution by the more anoxic conditions in the groundwater areas). For the felling/post-felling period, the calcium, magnesium, Gran alkalinity, Fe, Ni, Sr, and Ba concentrations continued to fall substantially, while the declines in the trace metals were smaller. Whether or not this fall was due to the introduction of the borehole, the fell or a combination of both, cannot be stated because of lack of sufficient information.

No sudden level or water quality change was observed for the control site borehole even though it was on the same side of the river and nearer to the deep borehole than that for the manipulation site on the opposite side of the river. Further, the occurrence of high alkalinity waters at shallow depths at the manipulation site was surprising as the effects of the soil inputs might be expected to dominate. Indeed, the production of more acidic waters at greater depths at the manipulation site as a result of the introduction of the deep borehole is both counter-intuitive and goes against the findings for deep boreholes in the area where alkalinity is associated with the hydrogeochemical gradient, increasing with depth (Neal *et al.*, 1997c). Thus, when the information from this study is combined with earlier studies of groundwaters at Plynlimon, the groundwater regime is extremely difficult to describe in detail due to the complex fracture flow pathways which dominate the hydrogeology

Table 5. Summary statistics for groundwaters at the control and manipulation sites. For both sites, the times corresponding to pre-fell and fell/post-fell times. The fell and post-fell data have been combined as there is an insufficiently long data record to allow proper separation. The fell/post-fell period represents a three year period starting with the commencement of fell. All concentrations are as 'atomic rather than species weight' except for the * terms ammonium (µg-NH_4 l^{-1}), sulphate (mg-SO_4 l^{-1}) and nitrate (mg-NO_3 l^{-1}).

		Control						Manipulation								
		Pre-fell			*Fell/post-fell*			*Early*			*Pre-fell*			*Fell/post-fell*		
		avg	*min*	*max*	*avg*	*min*	*max*	*avg*	*min*	*max*	*avg*	*min*	*max*	*avg*	*min*	*max*
Na	mg l^{-1}	6.12	5.29	9.09	5.97	5.27	6.94	7.33	6.75	7.95	5.44	4.61	6.19	4.63	3.25	5.99
K	mg l^{-1}	0.18	0.11	0.53	0.14	0.00	0.37	1.35	1.00	1.60	0.95	0.44	1.40	0.47	0.28	0.83
Ca	mg l^{-1}	1.54	1.00	5.00	1.41	1.06	1.95	22.68	21.23	24.39	12.74	3.73	20.51	4.08	1.19	12.19
Mg	mg l^{-1}	1.15	0.94	2.32	1.19	0.92	1.32	8.20	7.42	8.93	4.37	1.53	6.79	1.84	0.58	4.58
NH_4	µg* l^{-1}	35	0	122	18	0	84	87	32	174	60	10	122	45	8	480
Cl	mg l^{-1}	9.61	6.50	11.80	10.51	8.00	13.60	9.90	9.30	10.30	10.58	8.40	11.60	8.52	3.70	11.60
SO_4	mg* l^{-1}	6.87	5.03	37.68	5.32	4.71	8.93	4.13	3.66	4.53	5.72	2.32	16.09	5.11	3.24	9.53
NO_3	mg* l^{-1}	1.47	0.10	2.00	2.26	0.65	3.45	0	0	0	0	0	0	0.42	0	2.75
F	µg l^{-1}	69	30	100	47	0	100	73	60	100	63	30	100	47	0	90
Br	mg l^{-1}	18	15	30	16	12	24	37	32	41	35	14	64	53	21	103
I	mg l^{-1}	1.3	0.8	3.3	1.0	0.9	1.3	10.7	3.7	12.5	6.2	0.6	9.9	9.1	1.3	21.0
PO_4	µg-Pl^{-1}	2	0	40	10	0	70	1	0	10	5	0	60	16	0	110
DOC	mg l^{-1}	0.5	0	1.4	0.5	0	1.2	1.9	1.0	10.5	1.6	0.7	8.7	1.3	0.5	3.2
Si	mg l^{-1}	2.96	1.95	4.55	2.77	2.45	3.70	4.76	4.35	7.20	5.01	2.90	5.90	4.15	3.15	5.40
pH		4.86	4.28	5.30	4.81	4.72	4.97	6.49	6.37	6.58	6.03	5.12	6.48	5.56	5.13	6.33
GAlk	µeq l^{-1}	12	-109	89	7	-10	28	1934	1662	2293	886	37	1993	224	25	1061
Al	µg l^{-1}	160	23.2	848	197	76.2	362	3.7	0.8	8.2	20.5	0	194.8	21.6	3.9	93.9
B	µg l^{-1}	4.9	3.5	13.3	4.8	2.8	7.9	24.1	20.4	31.5	12.5	3.9	18.2	9.7	0.9	48.9
Ba	µg l^{-1}	6.6	4.1	29.3	7.0	4.5	19.6	20.8	18.7	31.4	13.5	6.5	21.1	7.1	4.1	11.7
Co	µg l^{-1}	2.2	0.9	19.8	2.7	1.8	4.9	4.9	4.2	6.3	4.6	2.5	8.2	4.5	1.6	8.7
Cu	µg l^{-1}	4.6	1.1	20.9	2.9	0.9	32.4	2.8	1.2	5.0	2.2	0.9	5.8	1.7	0.5	6.5
Fe	µg l^{-1}	110	4	3475	46	5	592	15023	9379	16701	6476	7	14505	5571	8	17199
Li	µg l^{-1}	3.6	2.8	6.3	3.7	2.7	6.6	13.7	12.1	15.4	11.4	3.7	15.3	7.3	3.8	12.1
Mn	µg l^{-1}	149	104	533	175	148	286	402	376	437	318	133	460	184	67	365
Ni	µg l^{-1}	7.4	4.1	30.3	6.6	4.8	22.0	89.2	56.9	115.0	41.2	3.9	81.8	32.0	3.5	79.6
Pb	µg l^{-1}	1.9	0.3	8.0	1.8	0.4	25.8	0.5	0	1.0	0.4	0	1.4	0.5	0.1	3.1
Rb	µg l^{-1}	0.4	0.2	1.1	0.4	0.3	0.7	3.7	3.4	4.3	2.6	1.2	3.5	1.3	0.8	2.1
Sr	µg l^{-1}	7.0	5.0	20.8	6.6	4.6	7.9	67.4	62.3	70.6	34.1	9.3	53.9	10.0	3.3	26.7
Y	µg l^{-1}	0.8	0.1	10.8	0.7	0.4	0.9	0.1	0.0	0.2	0.2	0.1	0.5	0.5	0.1	1.4
Zn	µg l^{-1}	29.7	15.7	83.7	41.0	18.1	174.9	38.8	18.3	82.9	45.8	22.5	103.6	75.6	23.7	300.2

and the high degree of spatial and temporal variation in groundwater hydrogeochemistry.

DISSOLVED CARBON DIOXIDE IN THE STREAMS AND GROUNDWATER

The relationship between pH and Gran alkalinity needs mention because there are marked differences for the groundwater and surface water systems as a consequence of contrasting amounts of dissolved CO_2. Dissolved CO_2 builds up within the soils and groundwaters due to respiratory processes by vegetation and micro-organisms and from the breakdown of organic carbon. Within the stream, there is the potential for this build-up of dissolved CO_2 to be dissipated partially by loss of gaseous CO_2 to the atmosphere from the stream surface. Higher CO_2 pressures

affect the inorganic carbon equilibrium in the water by increasing the dissolved carbonic acid (H_2CO_3) concentrations. The carbonic acid then partly dissociates into hydrogen and bicarbonate ions in equal measure ($H_2CO_3 = H^+ + HCO_3^-$). Thus, an increase in the partial pressure of CO_2 leads to decreased pH but no change in the Gran alkalinity as the H^+ and HCO_3^- generated in the process cancel each other out. At lower CO_2 pressures, pH increases due to lowering of both the H_2CO_3 concentration and the extent of its disassociation into hydrogen and bicarbonate ions.

The level of carbon dioxide can be assessed for the waters using information on the pH and Gran alkalinity (Neal *et al.*, 1998c), using the approximation that

$$EpCO_2\ H\bullet(\text{Gran Alkalinity} + 10^{6\text{-pH}})*10^{6\text{-pH}}/6.$$

For this equation, $EpCO_2$ is the extent of CO_2 saturation: values of $EpCO_2$ of 0.1, 1 and 10 correspond to a tenth saturation, saturation and ten times saturation, respectively, with reference to equilibrium with air. The Gran alkalinity has units of $\mu Eq\ l^{-1}$ and the $10^{6\text{-pH}}$ term is an approximation for the hydrogen ion concentration in the same units.

For the waters under consideration here, the methodology does not perform well at values of pH below 6 due to small errors in the pH measurement which are exaggerated at low pH. This is because the estimate of $EpCO_2$ is linked to (a) the small difference between Gran alkalinity and $10^{6\text{-pH}}$ at low pH, which can even lead to unacceptably negative values of $EpCO_2$, and (b) the exponential term in pH (Neal, 1988). For this study, only those waters with pH above 6 were used for the analysis, and the results are as follows.

The range in $EpCO_2$ levels in the groundwaters, for the control is 13 to 80 and for the manipulation site 83 to 139 times that of the atmosphere. These values are in the range observed for other groundwaters in the area (Neal *et al.*, 1997c)

Correspondingly, $EpCO_2$ levels in the main stem of the Nant Tanllwyth show lower degrees of saturation, but there are some notable differences both in terms of the upstream and downstream sampling points with respect to the introduction of the deep borehole which affected the stream chemistry as described earlier. Analysis of these upstream and downstream data mainly represents baseflow to moderate flows. It shows three main features. Firstly, the partial pressures of carbon dioxide vary between around zero and 28 times atmospheric pressure. Within the streams, a value of around the atmospheric level is to be expected; this means that some ground water has entered the stream and not fully degassed its high load of dissolved carbon dioxide that is present in groundwater systems. Secondly, there seem to be higher partial pressures of carbon dioxide late in the record (2001–2002). For the upstream site (i.e. not influenced by the deep borehole), the partial pressure of carbon dioxide averages 3.2 with a range of 0.4 to 16 times the atmospheric value, for the monitoring period 1991 to 2001 inclusive: for the period 2001–2002, the corresponding values average 8.2 with a range of 2.2 to 25. Thirdly, for the upstream site influenced by the deep borehole, the partial pressure of carbon dioxide averages 4.7 with a range of 0.5 to 28 times the atmospheric value, for the monitoring period 1991 to 2001 inclusive. For the period 2001-2002, the corresponding values average 7.2 with a range of 0.5 to 26.

Thus,

(1) The carbon dioxide laden water from the borehole has increased the dissolved carbon dioxide in the stream.
(2) A marked increase in carbon dioxide pressures in 2001–2002 does not seem to be linked directly to the felling in the sense that the timing of the increase does not correspond to that of felling or the response of other components to felling.
(3) Preliminary investigation for other streams in the area does not show a similar pattern of increase. The reason for this change is not clear.

Conclusion

In general, local runoff from the soils is highly acidic. However, in the main stem of the river, the chemistry is more varied. This reflects the range of inputs of water derived from acidic soil waters, predominant during high flows; as compared with the less acidic calcium and magnesium bearing groundwaters, predominant under baseflow conditions. Nonetheless, there is a large variation in both soil and groundwater chemistry. These broad patterns observed in the streams are 'classic', as is the occurrence of soil and groundwater with complex patterns of hydrogeochemical behaviour (Neal *et al.*, 1997b,d; Hill and Neal, 1997). With felling, a marked change in water quality is observed at the local scale. In particular, nitrate, phosphate and ammonium concentrations increase with felling and subsequently tail off over time. Correspondingly, there is a decline in sodium and chloride concentrations. Such patterns fit well with the standard view of the effects of felling as discussed earlier in the paper.

What was not expected was the lack of much of a trace of the felling effects within the chemistry of the main stem of the river, compared to that at the local scale. Potentially, this can mean that the data at the local scale are not representative. Indeed, there certainly is a strong case for saying that a large spatial range in water quality is associated

with the contrasting inputs of soil and ground waters (Hill and Neal, 1997; Neal *et al.*, 1997d; Foster *et al.*, 2001) and (where funds allow — which was not the case in the present study or many other studies) a proper statistical test with replication is strongly recommended. However, for forested systems in the area, as well as elsewhere, that have been clear-felled, there has been a universal effect shown at least for nitrate (Adamson *et al.*, 1997; Adamson and Hornung, 1990; Neal and Reynolds, 1998; Neal *et al.*, 1992a,b, 1997a, 2003c). Thus, for this study it seems that there may be some process, which removes nitrate, ammonium and phosphate generated by the felling, either near to or within the stream itself. For the Plynlimon area, the waters are extremely depleted in phosphate and phosphate is the limiting nutrient in such systems. Within the gleys, there is a much greater potential for the release of phosphate, which is bound to iron oxide phases in the soil, with felling. Within the soil near the river and within the river itself, there is the potential for such phosphate release to stimulate biological growth which, in turn, will lead to the removal of ammonium and nitrate species (Neal *et al.*, 2003d,e). It is proposed that this process is occurring, and further research on this is strongly recommended because it may well prove to be an important factor to include in environmental impact modelling for such systems.

In relation to management practices, the present work on the felling effects on stream water quality clearly provides very good news because in the main stream very little effect of environmental concern seems to have occurred. Indeed, the water quality has simply improved as there is a net uptake in nitrate. This feature has been observed in other catchments subjected to felling, but usually at a later date when the newly developing vegetation takes increasing amounts of nitrogen into the growing biomass (Neal, 2002a,b).

The results illustrate an important feature of making measurements at scales representative of the more important management level, the catchment, where, for example, the effects at the local scale simply do not reflect the changes at what is currently perceived at the local hill slope scale. Thus, if only the plot scale data produced in this paper were considered, greater concerns over ammonium and phosphate release might have been expressed. Nevertheless, small scale plot results may be ecologically important for the life stages of some organisms. For example, felling may have an important effect on pond chemistry and biology (e.g. frog populations). So, there is a need for caution as to impacts as their importance depends critically on the biological target.

The most significant conclusion both in terms of process understanding and environmental management is that there is little change in stream acidity with felling. This implies that the catchment has a great ability to dampen down changes in acidity that can potentially occur with changing anion concentrations and land manipulation. The groundwater results (including the longevity of stream water quality improvement with the introduction of the deep borehole by the Tanllwyth) indicate a potential for counteracting, at least in part, the acidification of the streams and soils. The complexity of flow pathways and flux attenuation of pollutants has been highlighted in this study and elsewhere. This means that new modelling frameworks, particularly with regards to fractal processing, are needed to describe the processes occurring. These modelling frameworks are specifically required to address environmental management issues such as sustainability of forestry resources and the impacts of climate change, land use change and climate instability.

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