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Stream water quality in acid sensitive UK upland areas; an example of potential water quality remediation based on groundwater manipulation.

Colin Neal[1], Timothy Hill[1], Sarah Alexander[2], Brian Reynolds[2], Susan Hill[1], Andy J. Dixon[1], Martin Harrow[1], Margaret Neal[1], and Christopher J. Smith[1].

[1] Institute of Hydrology, Maclean Building, Crowmarsh Gifford, Wallingford, OXON, OX10 8BB.
[2] Institute of Terrestrial Ecology, Bangor Research Unit, University College, Deniol Road, Bangor, Gwynedd, N. Wales, LL57 2UP.

Abstract

The patterns of variation in water quality for an acidic stream draining plantation forest overlying acidic and acid sensitive gley soils with shale and slate bedrock changed following the introduction of a 45 m deep borehole near to the stream. During drilling, air flushing of debris from the borehole cleared fracture routes for groundwater penetration to the stream via the stream bed. Consequently, there were and there remain marked increases in pH, alkalinity and calcium concentrations in the stream water. The extent of this water quality improvement varies according to flow. Under extreme highflow conditions, most of the stream water is supplied from near surface soil water sources and acidic stream waters (pH about 4.2) result. Under baseflow conditions, the stream water pH is about 7.0 upstream and about 7.5 downstream of the borehole. Under intermediate flow conditions, the improvement in pH is most marked and values increase from around 5 to around 6.3.

For acid sensitive 'hard rock' areas such as those studied here, the bedrock has frequently been assumed to be both impermeable and low in base cations. This study illustrates that this view may be incorrect, and that groundwater may provide an important modifier of streamwater quality, at least for slate and shale dominated hard rock areas. Indeed, the work demonstrates clearly the potential for water quality remediation through groundwater manipulation.

Introduction

Much of upland Britain is acidic and acid sensitive and considerable concerns have been raised over the impacts of acidic deposition, conifer afforestation and harvesting on stream biota (Stoner and Gee, 1985; UKAWRG, 1988; Nisbet, 1990; Neal *et al.*, 1992*a,b*). These areas are ecologically vulnerable due to the presence of thin acidic and acid sensitive soils that overlie relatively base-deficient bedrock (Edmunds and Kinniburgh, 1986; UKAWRG, 1988). However, the acidity of stream runoff in the British uplands varies considerably with flow and baseflow waters tend to be much less acidic and more base enriched than stormflow (UKAWRG, 1988; Neal *et al.*, 1990*a,b*; Davies *et al.*, 1992). This feature implies that, within the catchments, there are hydrochemically distinct sources contributing to stream flow generation. For the soils, cation exchange reactions and organic acid production modify the wet and dry deposition inputs leading to acidic soil waters enriched in aluminium. Correspondingly, within the lower soils (about 0.5 to 1m depth) and shallow groundwater areas (<15m depth), weathering reactions involving silicate and carbonate materials in the bedrock neutralize the acidity, so that much of the aluminium generated in the soils is precipitated. Variations in stream water quality have thus been linked to the relative contributions of acidic soil waters and base enriched and more alkaline groundwaters (Christophersen *et al.*, 1990; Hooper *et al.*, 1990; Neal *et al.*, 1990*a,b*; Robson *et al.*, 1990). However, the common view within the environmental sciences has been that the Lower Palaeozoic slate and shale bedrock typical of the Welsh uplands and southern Scotland is relatively impermeable even though it is well known that the rock is highly fractured and that regional water quality is often linked to geology and hydrogeology (Bricker and Rice, 1989). Unfortunately, there have been very few studies of groundwaters in these upland areas and the extent of groundwater supplies to stream flow and stream water quality is uncertain (Edmunds and Savage, 1991; Cook *et al.*, 1991; Edmunds and Key, 1996). Nonetheless, within hydrogeological and water resource research, the study of fractured hard rock areas is expanding in importance (Banks and Banks, 1993). Even in the early 1900s, the water resource potential of slates was recognised; Clapp (1911) wrote 'Investigations of the underground waters of Maine in 1906 have shown that in the state the slates contain more water than any other kind of rock, and that where they do not contain lime in detrimental quantities their water is the best found in the state'. Furthermore, a study of the granitic Loch Fleet catchment showed that inputs of approximately 5% of relatively alkaline groundwaters were potentially extremely important in buffering the effects of acid deposition (Cook *et al.*, 1991).

Recently, a pilot study has been undertaken within the upper river Severn (Afon Hafren) catchments in mid Wales (Neal *et al.*, 1997) to assess the presence or absence of groundwater. The study sites are typical of many parts of the British uplands in relation to those areas with thin acidic soils and slate and shale bedrock. The study area is particularly appropriate for such work as stream chemistry has been monitored for several years and stream water hydrograph splitting indicates large contributions from groundwater (Neal *et al.*, 1990a,b). As part of this pilot study, three deep boreholes were drilled near the main upper Severn tributaries to explore potential groundwater sources and to look at geochemical gradients with depth.

In the case of the most acidic tributary of the upper River Severn, the Nant Tanllwyth, drilling of a deep borehole opened bedrock fracture routes to the river. A major improvement in stream water quality resulted due to increased supply of base rich groundwaters of high alkalinity. This paper shows that (a) groundwaters can provide an important contribution to water quality in these acidic upland areas, (b) the bedrock contains sufficient bases to provide good quality high alkalinity waters and (c) there is potential for water quality remediation based on groundwater manipulation.

Study area, sampling and analysis

The work presented here relates primarily to two subcatchments of the Upper Severn in mid Wales, the Nant Tanllwyth, one of the smaller tributaries and the Afon Hafren, one of the main headwater rivers in the Plynlimon area (Figure 1). The sites are located about 24 miles inland from the west coast of mid Wales.

The Plynlimon area forms part of a deeply dissected plateau, much of it over 450 m, rising to 750 m on the summit, Pumlumon Fawr. The upland massif, on which Plynlimon lies, is composed of lower Palaeozoic rocks (mudstones, greywackes, sandstones and grits; Breward, 1990; Robson, 1993). The oldest of the exposed beds are quartzose grits overlain by blue-grey mudstones and these occur in the upper parts of the Plynlimon area, forming the core of an anticlinal structure. The lower slopes comprise mainly younger mudstones and shales which are pyritic bearing.

The soils in the area are thin, typically 70 cm thick, organic rich and acidic (pH typically about 4). They comprise a mosaic of stagno-podzol, peat, brown earth and stagno-gley units within the sub-catchments. The upper 48% of the Afon Hafren catchment (347ha), above the conifer plantation line, comprises acid grassland and peat moorland; on the remaining 52%, plantation forestry (predominantly Sitka spruce, *Picea sitchensis*) was established, in various phases between 1937 and 1964. The Nant Tanllwyth catchment (97 ha) is 100% forested, trees having been planted onto acid moorland at about the same time as the rest of the Hafren catchments, and the predominant soils are gleys. The Afon Hafren is used here as a control for changes on the Tanllwyth.

The altitude range for the catchments is about 360–470 m. Rainfall averages about 2500 mm/yr and evaporation and transpiration typically amount to around 500–700 mm/yr. For both the Nant Tanllwyth and Hafren catchments, the streamflow responses to storm events are similar in shape and timing, the hydrograph response to storms being both rapid and 'flashy'.

For the Tanllwyth site, a 45 m deep 90 cm diameter borehole (VB3) was introduced in May 1994 about 5 m from the main stream using a top drive hydraulic rotary drilling rig with a rock roller bit down to bedrock and a pneumatic down the hole hammer technique within the bedrock. Both techniques used a 250 cfm/100 psi compressor for flushing rock debris. Within the bedrock, drilling revealed a grey mudstone to a depth of 10 m and a dark grey mudstone below this level. The overburden was cased off to a depth of 3 m with 117 mm diameter steel casing. Below this depth, the borehole was left open for geophysical logging.

Weekly sampling of the Afon Hafren began in May 1983. For the Nant Tanllwyth, sampling began in August 1991 at a site just upstream of one of the Institute of Hydrology's gauging structures (Figure 1). This location is about 20 m downstream of the subsequently introduced borehole (VB 3, Figure 1). Following borehole installation and the identification of a marked change in stream water chemistry, an additional sampling site about 50 m further upstream of the borehole was established in August 1994 (*cf.* Neal *et al.*, 1997). Within the remaining text, the lower, long term, monitoring site is designated as the 'Tanllwyth' site while the upper, more recent, sampling location is designated as the 'Tanllwyth Bridge' site. Stream water sampling continues.

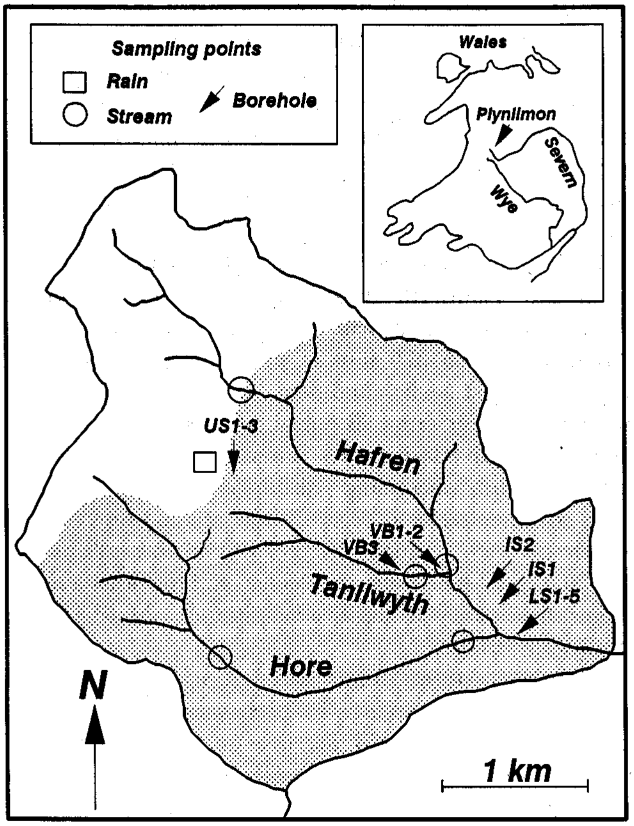

Fig. 1 *The upper River Severn study area. The boreholes are listed according to four types of location within the Hafren catchment: 'US' for the upper plateau-edge; 'IS' the intermediate-gradient slopes; 'LS' the lower slopes near to the river; 'VB' the valley bottom area very close to the stream.*

Stream water was collected by 'grab sampling' and was filtered immediately on collection. After filtration, the samples were stored and analysed as follows (cf. Neal *et al.*, 1992*a*). Samples filtered through 0.45 μm membranes were stored at 4 °C in the dark in HCl acid-washed polypropylene bottles with aristar HNO_3 (1% v/v). These samples were analysed using inductively-coupled optical emission spectroscopy and inductively-coupled mass spectrometry, for major, minor and trace metal levels. Samples filtered through 2 μm glass fibre filters and stored in chromic acid-washed glass bottles (also in the dark at 4 °C), were analysed using automated colorimetric techniques for silicate and several major and minor anions. Dissolved organic carbon was determined using a TOCsin II aqueous carbon analyser. Alkalinity and pH were determined on unfiltered samples using electrometric techniques. For the titrations, to minimise interferences, reagents, electrodes and water samples were maintained at river temperature. CO_2 degassing was minimised by storing the samples in sealed, filled, glass bottles (Neal, 1988). Two alkalinity measurements based on acidimetric Gran procedures were made, one for the pH range 4.5–4.0 and the other from 4.0–3.0. The titration in the higher pH range (Alk_{Gran1}) corresponds approximately to an estimation of bicarbonate acidity buffering while the lower range (Alk_{Gran2}) includes organic acid buffering. As both Gran alkalinity measurements are very similar, for this contribution only one of them (Alk_{Gran1}) is referred to.

From 19th June until 30th September 1995, stream water samples were collected daily from the Hafren and Tanllwyth sites. On return to the laboratory, pH and alkalinity were measured on an unfiltered subsample whilst Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, Cl^-, NO_3^- and NH_4^+ were determined using a Dionex ion chromatograph after filtration through 0.45 μm membrane filters. Total monomeric aluminium was determined on a filtered subsample using the pyrocatchecol violet technique of Dougan and Wilson (1974).

Results

Both the Hafren and Tanllwyth streams show considerable water quality variation with flow. As for many upland areas, stormflow is marked by acidic and aluminium bearing stream waters, while baseflow is less acidic and low in aluminium but enriched in bicarbonate and base cations (Table 1). While the Tanllwyth and Hafren baseflow chemistries are similar, due to very similar slate and shale bedrock types, the Tanllwyth is more acidic than the Hafren at stormflow due to differences in hydrological pathways for the contrasting gley and podzolic soil types (*cf.* Boggie and Knight, 1980; Pyatt *et al.*, 1985; Soulsby, 1992). For the Tanllwyth, the soils are peaty gleys; consequently, they have an impermeable clay below the upper soils which are organic rich and highly acidic. Thus, for the Tanllwyth, there is a very large

Table 1. Major ion chemistries for baseflow and stormflow waters of the Tanllwyth, prior to borehole introduction, and Afon Hafren. All units are mgl^{-1} except for alkalinity (μEql^{-1}) and pH. High flow and low flow correspond with values greater than 0.1 mm/15 min and less than 0.01 mm/15 min.

	Afon Hafren		**Tanllwyth**	
Element	**Base flow**	**Storm flow**	**Base flow**	**Storm flow**
Na	3.9	3.9	5.2	4.4
K	0.1	0.2	0.2	0.2
Ca	1.0	0.8	2.3	0.7
Mg	0.8	0.8	1.1	0.7
Total Al	0.1	0.4	0.1	0.6
DOC	0.8	2.2	1.0	1.9
Cl	6.8	7.2	9.1	8.0
SO_4	3.5	4.7	5.9	5.3
NO_3	0.8	1.7	1.7	2.4
Alk_{Gran1}	24.2	–28.3	43.7	–56.6
pH	6.3	4.6	6.4	4.3

near surface runoff component during storm events and groundwater residence times might be long. In contrast, the Hafren has more permeable podzolic soils. There is, therefore, the possibility of deeper water circulation, shorter groundwater residence times and less acidic soil waters. In addition, the concentrations of Na, Cl and SO_4 are higher for the Tanllwyth than for the Hafren. This difference reflects both the increased evapotranspiration and atmospheric capture and dry deposition of pollutants for the Tanllwyth due to the higher proportion of tree cover (Neal, 1992*a*).

During the installation of the Tanllwyth borehole, loss of air-flush circulation resulted in the opening of groundwater fracture routes to the stream. This was manifest by observation of the stream bed near the borehole which was described by the drillers as 'fizzing like a jacuzzi'. Subsequently, brown precipitates were observed on the stream bed and, at low flows, they have continued to be observed, unabated, at the same location, up to the time of publication. In terms of hydrological activity in the borehole, water level measurements have always shown a positive head relative to the adjacent stream (usually >1 m of head). It therefore seems that there was a continued supply of groundwater to the stream throughout the sampling period. Further, during the winter period, the borehole became artesian with very high outflows: artesian conditions remained for a few days after the rainfall event. Hence, the borehole had to be capped.

There was a marked difference in stream water chemistry before and after borehole introduction for the Tanllwyth but no discernable difference for the Hafren. For the Tanllwyth, differences were marked only for base cations, alkalinity and pH which all increased in concentration (Fig. 2): there was a smaller increase in silicate. Over the year, these changes remained constant without any decline. Plots of concentrations for various determinands (Fig. 3) measured at the two sites, before borehole installation, showed linear features indicating that the Afon Hafren was a suitable control. After borehole installation, the same linear pattern was observed for all the components which did not increase on the Tanllwyth following borehole installation. In contrast, a curve, two straight line segments or scattered relationships were observed for several of the base cations, Li, Mg, Ca, Sr, Ba, alkalinity, pH and silicate, which deviated from the linear pattern observed for the data prior to the borehole installation. The differences were greatest at intermediate to high values (ie intermediate to low flow conditions) when groundwater/borehole levels were high.

The chemistry at the Tanllwyth and Tanllwyth bridge sites show a similar contrast to that between the Hafren and the Tanllwyth after borehole introduction (Table 2). At baseflow, pH and calcium concentrations were lower upstream of the borehole by a factor of 0.5 pH units and a factor of a half to a quarter for base cations (Li, Mg, Ca, Sr, Ba). Indeed, the characteristic changes were associated mainly with baseflow chemistry and solely for those components associated with weathering (base cations and alkalinity). For stormflow, the main differences were for a) calcium, which was about 30% lower at the bridge site, b) alkalinity, which was more negative at the bridge site and c) pH, which was 0.4 units lower at the bridge site. The chemistry upstream at the bridge site was very similar to that observed prior to the introduction of the borehole. Plots of pH data for the Tanllwyth and Tanllwyth Bridge sites showed a maximum discrepancy at intermediate pH values (Fig. 4) with differences of 1–1.5 pH units at pH 5 for the bridge site: under the most acidic conditions, differences in pH were insignificant. For Gran alkalinity, plots for the Tanllwyth and Tanllwyth Bridge sites showed an increasing discrepancy with increasing alkalinity above $-20\ \mu Eq\ l^{-1}$ (Fig. 5): there seem to be two linear relationships, one of which showed a small discrepancy at low alkalinities ($<-20\ \mu Eq\ l^{-1}$ for Tanllwyth Bridge) and the other a much larger discrepancy at higher alkalinities ($>-20\ \mu Eq\ l^{-1}$ for Tanllwyth Bridge).

Numerous storm events were recorded during the period of daily sampling. In both streams, these were characterised by a rapid decrease in stream water pH with increasing flow, with similar minimum values of about pH 4.5 recorded at peak flow (Fig. 6). This pH was very close to values observed in small ephemeral forest drainage ditches within the peaty gley soils which flowed only during the rainfall events (Table 3). Recovery of pH during storm flow recession was more rapid in the Tanllwyth than in the Hafren, presumably reflecting the influence of the groundwater inputs. Storm events were also associated with a decline in divalent base cation concentrations (Fig. 6), although even at peak flows, calcium concentrations in the Tanllwyth were often at least $1 mgl^{-1}$ greater than in the Hafren. In both streams, aluminium concentrations increased with flow, with maximum storm event values in the Tanllwyth exceeding those in the Hafren (Fig. 6). As with pH, the highest recorded aluminium concentrations were similar to, or even greater than, those measured in the ephemeral drainage ditches (Table 3). Note that the very high flow values given in Table 3 differ from those in Table 1 because more extreme events have been captured with the more intensive sampling.

Hydrograph splitting to assess groundwater flow contributions to Tanllwyth stream flow generation

In terms of the volumetric contribution of groundwater to streamflow generation, the hydrograph splitting method was used here, following the method of Neal *et al.* (1990*a*, 1992*b*). For the Tanllwyth Bridge site, the Gran alkalinity was measured for near-surface runoff as

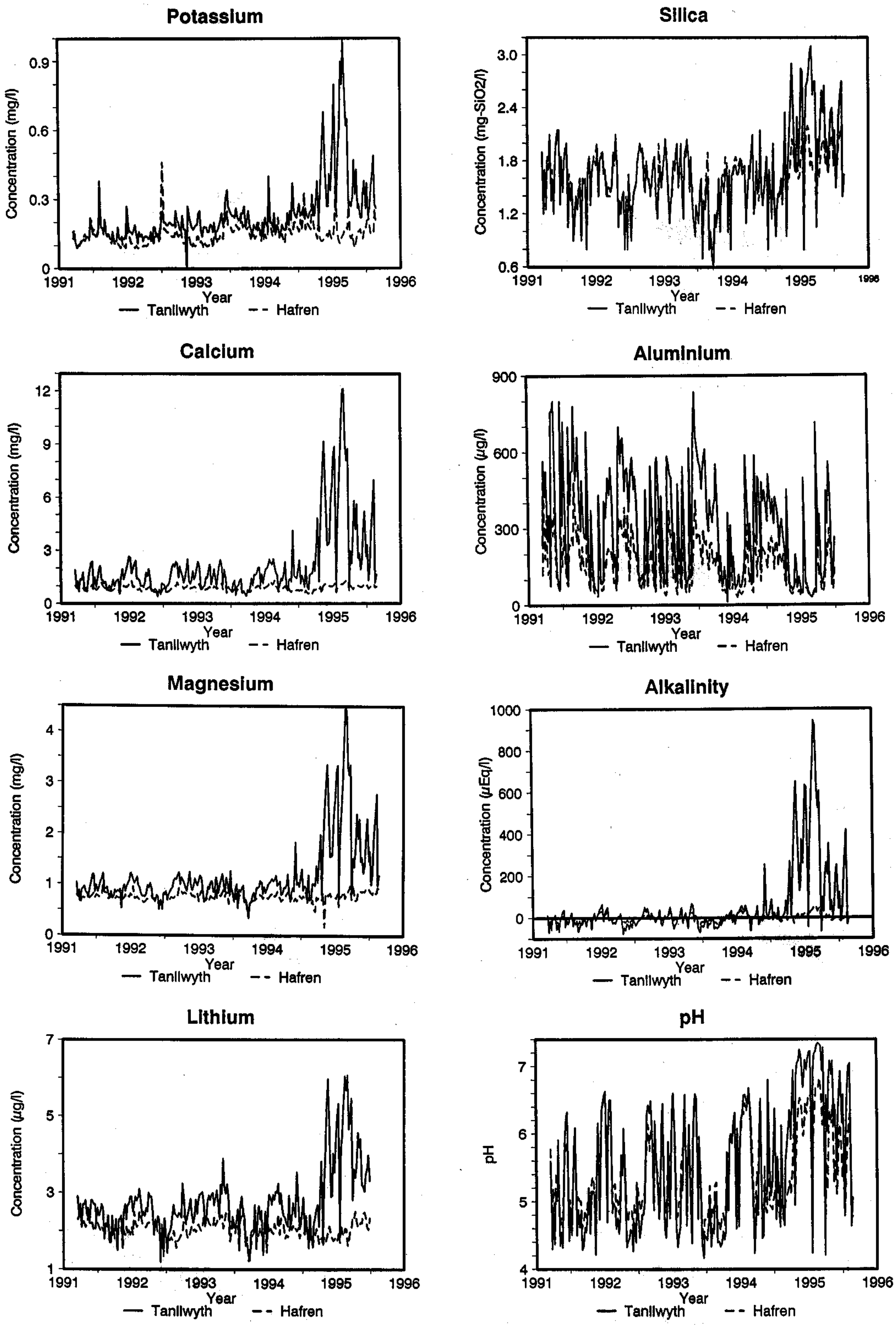

Fig. 2 *Time series plots for K, Ca, Mg, Li,* SiO_2*, Al,* Alk_{Gran1} *and pH for the Afon Hafren and Nant Tanllwyth: the Tanllwyth borehole was introduced in May 1994.*

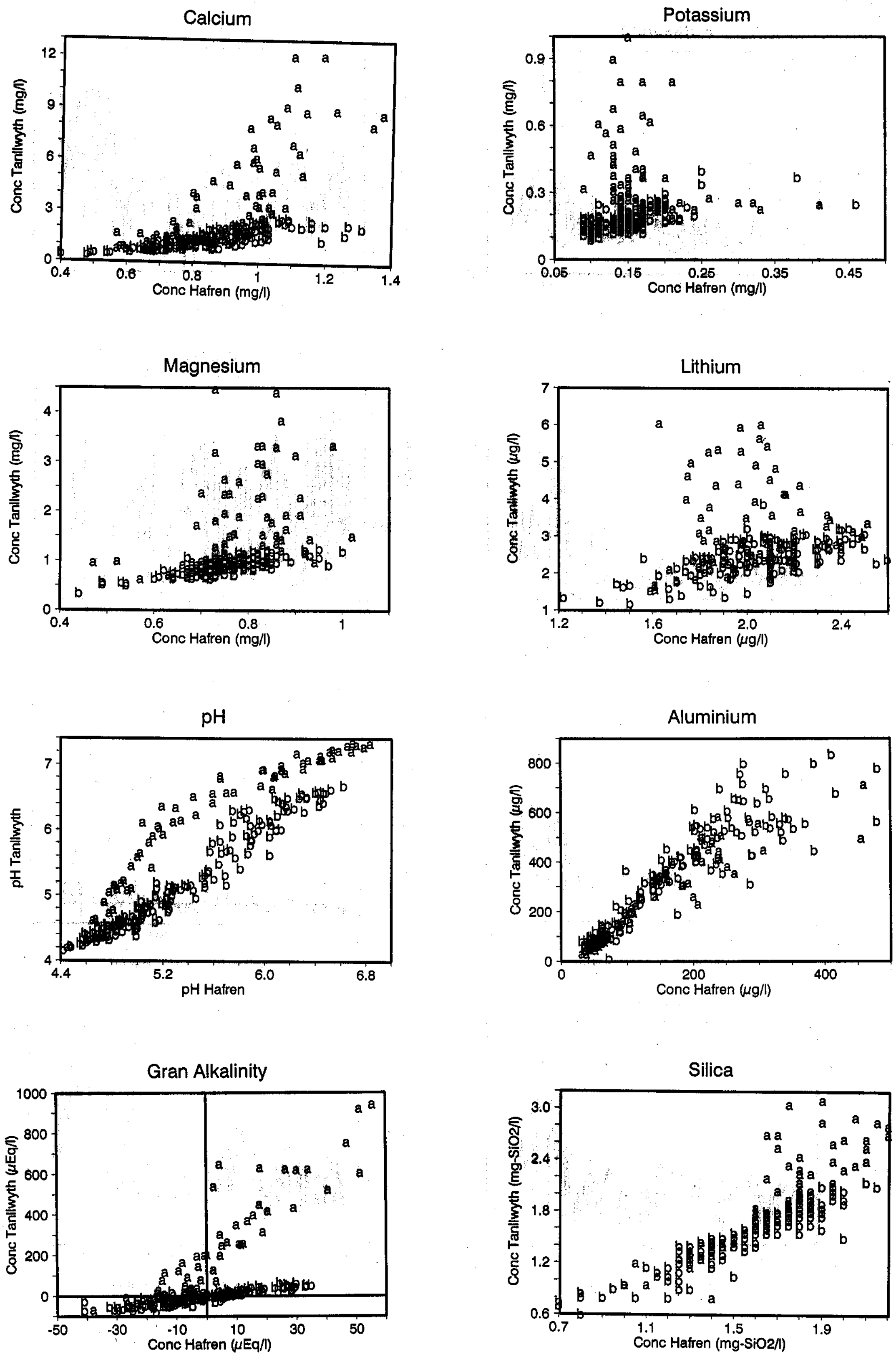

Fig. 3 *Plots of K, Ca, Mg, Li, SiO_2, Al and Alk_{Granl} concentrations and pH for the Afon Hafren and Nant Tanllwyth before (b) and after (a) borehole installation.*

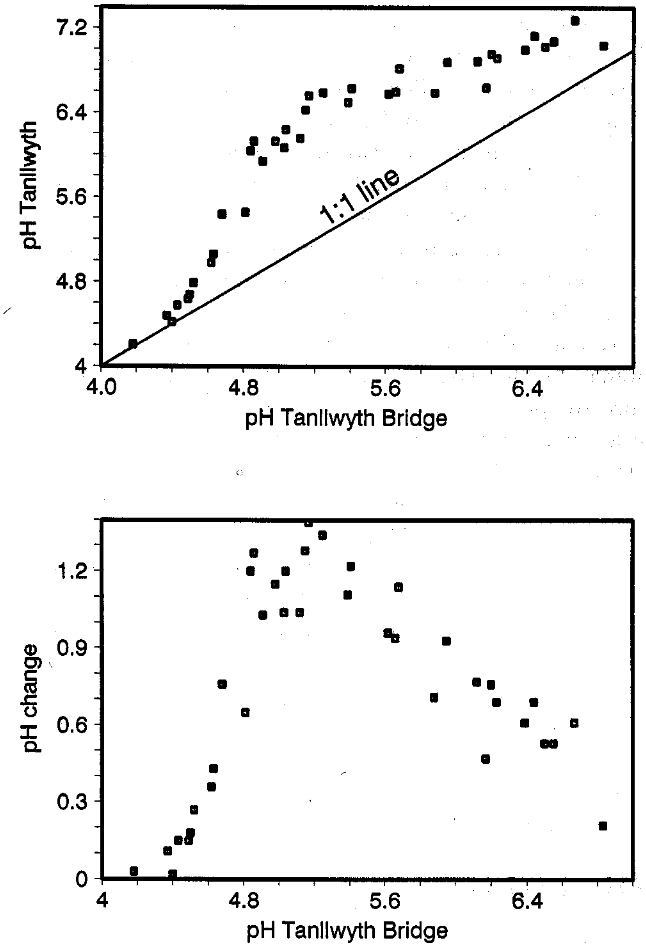

Fig. 4 *Comparative plots of (a) pH at the Tanllwyth and Tanllwyth Bridge sites and (b) the pH difference between the Tanllwyth and Tanllwyth Bridge sites and the pH at the Tanllwyth Bridge site.*

part of a study of the effects of deforestation on stream water quality (Neal *et al.*, 1992*b*); the average value (–79 μEq l^{-1}) was used to define the soil endmember. For the groundwater endmember, the average baseflow chemistry of the Tanllwyth stream at the bridge site was used (80 μEq l^{-1}). Results of the hydrograph splitting method showed that the proportion of groundwater decreased in an inverse or exponential decay fashion with increased flow (Fig. 7). At low to moderate flows, the groundwater proportion is in the range 50 to 100% while at the highest flows the groundwater contribution to total flow is insignificant. Despite this, the contribution of groundwater to the total flow increased with increasing flow and levelled off at the highest flows (Fig. 8). Thus, rainfall events increased the soil-water contribution to stormflow to a greater degree than the groundwater, resulting in a decrease in the proportion of groundwater contribution to the mix.

With regard to the new borehole-induced groundwater contribution to stream flow generation at the Tanllwyth site, a similar exercise was undertaken. This was possible since the alkalinity of the borehole water is about 3500 μEq l^{-1} and this has been used as the induced groundwater endmember value. The Gran alkalinity, however, varied between 1500–4000 μEq l^{-1} and there were insufficient data on the change in Gran alkalinity with flow for this borehole to allow for changing endmember composition. Also, the borehole samples were not pumped prior to sampling so the sample collected may not be truly representative of the water entering the stream. The hydrograph separation showed a volumetric contribution of newly induced groundwater of about 13% at baseflow which decreased with increasd flow (Fig. 7). These changes were similar to those for Tanllwyth Bridge except that (a) the declines in the percentages groundwater in the stream as flow increased were much steeper for the newly induced groundwater and (b)

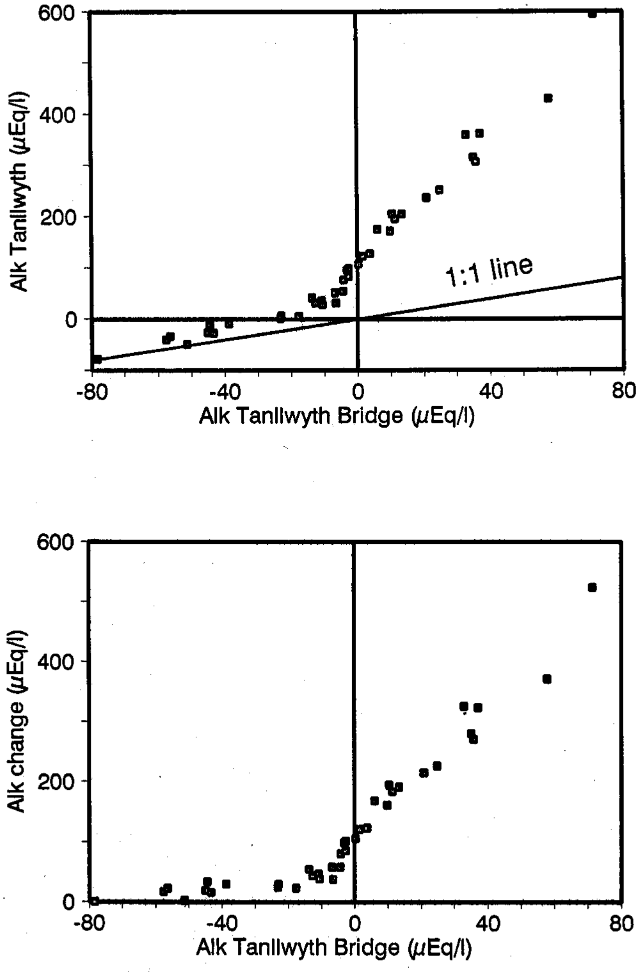

Fig. 5 *Comparative plots of (a) Alk_{Granl} at the Tanllwyth and Tanllwyth Bridge sites and (b) the Alk_{Granl} difference between the Tanllwyth and Tanllwyth Bridge sites and Alk_{Granl} at the Tanllwyth Bridge site.*

Table 2. Average major and trace element chemistries for the Tanllwyth Bridge and Tanllwyth sites upstream and downstream respectively of the deep borehole site; data collected between 19 October 1995 and 1 March 1996.

Species	Units	Tanllwyth baseflow	Tanllwyth Bridge baseflow	Tanllwyth stormflow	Tanllwyth Bridge stormflow
Na	mgl^{-1}	5.8	5.1	5.1	5.0
K	mgl^{-1}	0.49	0.21	0.25	0.23
Ca	mgl^{-1}	6.5	2.5	1.6	1.2
Mg	mgl^{-1}	2.6	1.2	1.1	1.0
SO4	mgl^{-1}	6.1	6.4	6.7	6.7
SiO_2	mgl^{-1}	2.6	2.2	1.6	1.5
DOC	mgl^{-1}	1.5	1.6	4.0	3.9
NO3	mgl^{-1}	2.2	2.5	4.2	4.3
Mn	μgl^{-1}	161.0	104.0	98.0	93.0
Fe	μgl^{-1}	215.0	219.0	202.0	202.0
Al	μgl^{-1}	85.0	95.0	600.0	651.0
Ni	μgl^{-1}	2.7	2.7	4.3	4.7
Co	μgl^{-1}	2.5	2.6	6.1	7.2
Zn	μgl^{-1}	12.0	10.0	31.0	30.0
Sr	μgl^{-1}	23.0	8.0	7.0	6.0
Ba	μgl^{-1}	8.2	3.7	7.4	6.7
Pb	μgl^{-1}	0.17	0.11	1.11	1.21
pH		7.1	6.6	5.0	4.6
Alk	μEql^{-1}	390.0	42.0	–14.0	–37.0

Table 3. Mean and range of pH, calcium and aluminium concentrations in forest ditches draining peaty gley soils in the Tanllwyth catchment.

Ditch		pH	Ca mgl^{-1}	Al mgl^{-1}
Tanllwyth North	Mean	4.03	1.43	0.35
	Range	3.86–4.82	0.29–3.03	0.16–0.49
Tanllwyth South	Mean	4.10	1.13	0.47
	Range	3.95–4.38	0.09–3.04	0.34–0.56

the contribution of this newly induced groundwater to total stream flow was, of course, lower.

The chemical hydrograph estimate of the newly induced groundwater flow contribution during storm events indicated a decline with increasing stream flow (Fig. 8). This is contrary to the results for the Tanllwyth Bridge site and it is opposite to what would be expected intuitively: increasing the head of water within the soils should promote the flow of induced groundwater. However, the hydrology of such areas is complex as, for example, transient perched saturation in the upper soil profile can occur during rainfall events even though the subsoil is unsaturated. None the less, as the chemistry of the borehole changes with time, it is reasonable to infer that there is a sufficiently large change in the induced groundwater endmember composition to affect the reliability of the estimated proportion of groundwater in stream stormflow. This inference is backed up, for the Tanllwyth Bridge and Tanllwyth sites, by the Gran alkalinity plots which show two intersecting lines rather than a single straight line: this feature indicates at least a three endmember mixing regime.

Accurate assessment of dependence of the induced endmember composition on stream flow cannot as yet be made. However, an approximate estimate can be given if it is assumed (a) that the percentage of induced groundwater to the stream water at the Tanllwyth site is directly proportional to the percentage of groundwater calculated for the Tanllwyth Bridge site and (b) that the estimate of the groundwater contribution at the Tanllwyth bridge site is correct. To do this, the standard mixing equations are applied but the groundwater endmember is taken as a variable rather than a constant and the proportion of induced groundwater is taken as 13% of the proportion of groundwater associated with the Tanllwyth Bridge site. The results of this exercise (Fig. 9) indicate that, with increasing flow, the Gran alkalinity decreases rapidly at relatively low flows and levels off at intermediate to high flows at about 500 μEq l^{-1}: this corresponds to a soil water contribution to the induced groundwater of about 84%.

Discussion

For many years hydrogeochemists have remarked on the important role of geology and hydrogeology in determining stream water chemistry even for hard-rock areas (Drever, 1982; Bricker and Rice, 1989; Cook *et al.*, 1991; Edmunds and Savage, 1991; Edmunds and Key, 1996). Despite this, for acidic and acid sensitive areas, little thought has been given to the potential value of groundwater manipulation to improve stream and lake water quality. Rather, environmental management in these impacted areas has often been focused on direct liming of catchments and stream courses even though environmental damage may result from such activities (Howells and Dalziel, 1991; Dise *et al.*, 1994).

The present study advances the research in chemical hydrograph splitting, hydrogeochemical understanding and environmental management by showing, for the Plynlimon catchments, that:

1) groundwater of high alkalinities occurs within the catchments and this groundwater influences stream water chemistry;
2) groundwater can be supplied to the stream to improve stream water quality without the cost of groundwater pumping;
3) groundwater of good quality can be supplied directly to that area of the stream, the stream bed, which is of critical biological importance: it is here where

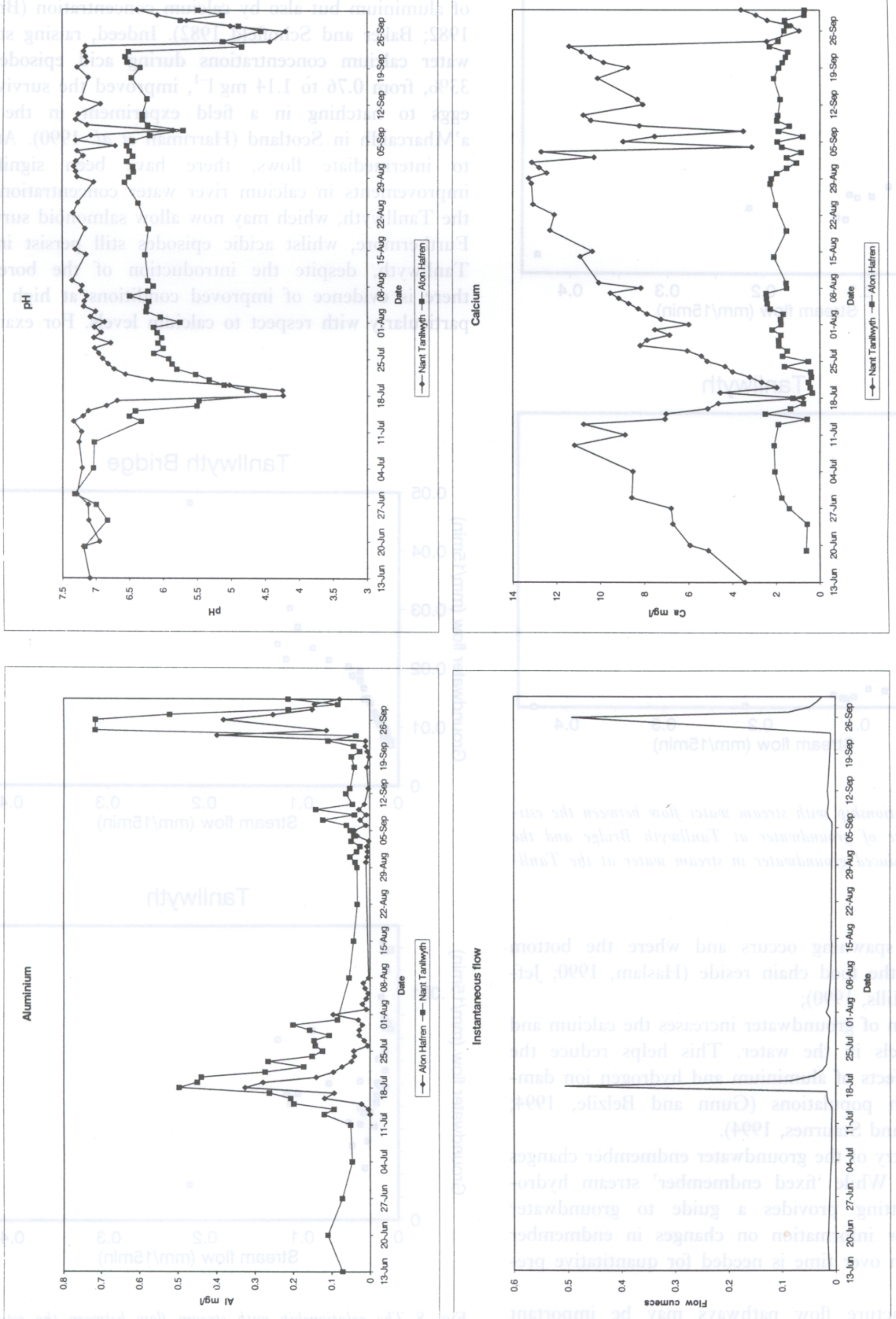

Fig. 6 *Time series plots of instantaneous stream flow, and daily pH, calcium and aluminium concentrations in the Tanllwyth and Hafren streams.*

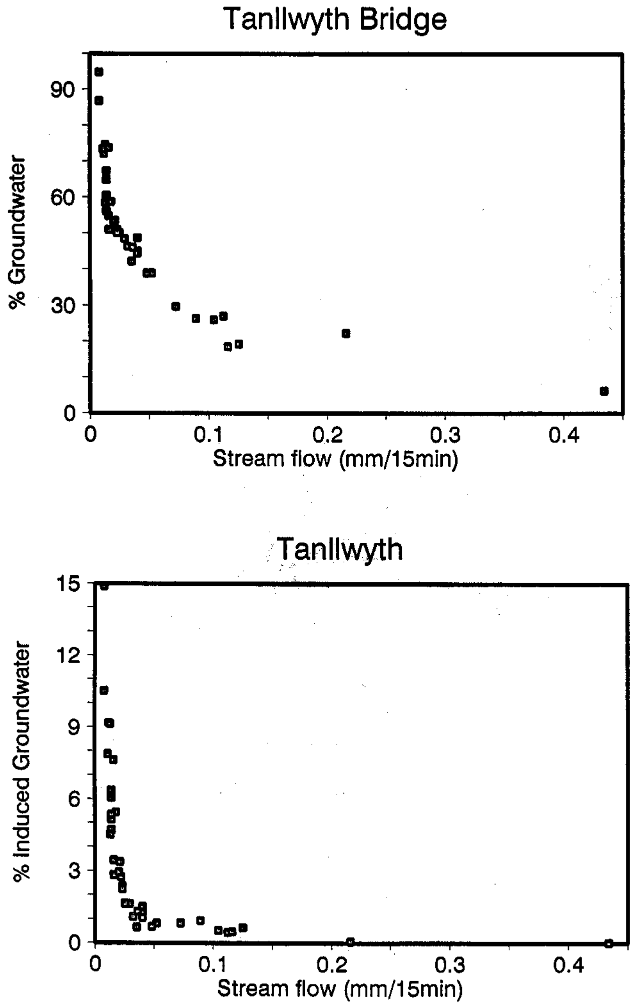

Fig. 7 *The relationship with stream water flow between the estimated percentage of groundwater at Tanllwyth Bridge and the percentage of induced groundwater in stream water at the Tanllwyth site.*

salmonoid spawning occurs and where the bottom feeders in the food chain reside (Haslam, 1990; Jeffries and Mills, 1990);

4) introduction of groundwater increases the calcium and silicate levels in the water. This helps reduce the harmful effects of aluminium and hydrogen ion damage to fish populations (Gunn and Belzile, 1994; Rosseland and Staurnes, 1994).
5) the chemistry of the groundwater endmember changes over time. While 'fixed endmember' stream hydrograph splitting provides a guide to groundwater inputs, new information on changes in endmember composition over time is needed for quantitative predictions.
6) shallow fracture flow pathways may be important hydrologically in transporting acidic surface waters rapidly to the stream during storm events.

Numerous field and laboratory studies have shown that the survival of juvenile salmonids in headwater streams is influenced not only by pH and the ionic forms of aluminium but also by calcium concentration (Brown, 1982; Baker and Schofield 1982). Indeed, raising stream water calcium concentrations during acid episodes by 33%, from 0.76 to 1.14 mg l^{-1}, improved the survival of eggs to hatching in a field experiment in the Allt a'Mharcaidh in Scotland (Harriman *et al.* 1990). At low to intermediate flows, there have been significant improvements in calcium river water concentrations for the Tanllwyth, which may now allow salmonoid survival. Furthermore, whilst acidic episodes still persist in the Tanllwyth, despite the introduction of the borehole, there is evidence of improved conditions at high flows particularly with respect to calcium levels. For example,

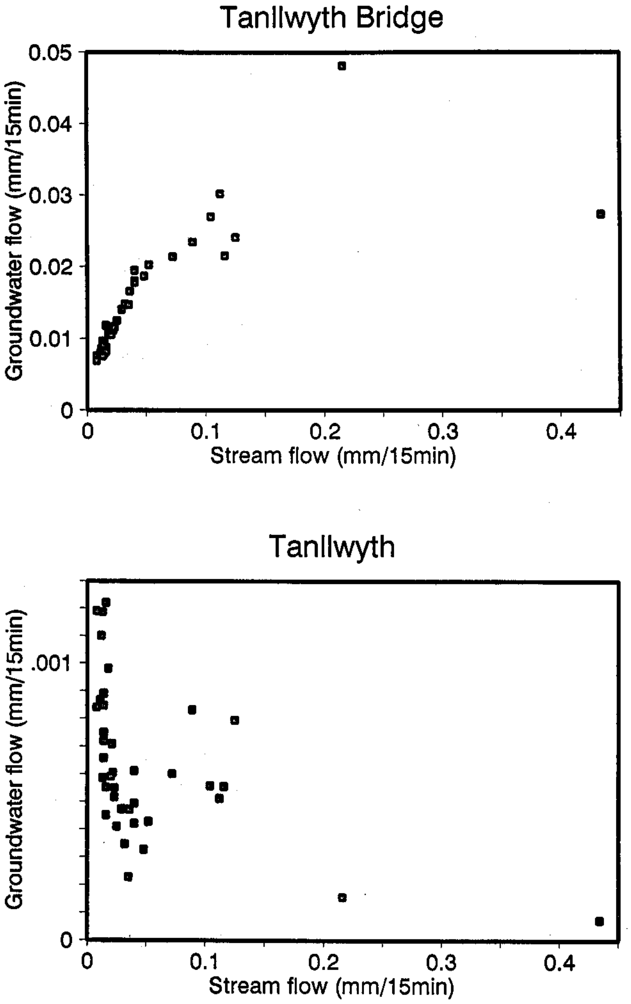

Fig. 8 *The relationship with stream flow between the estimated groundwater flow at Tanllwyth Bridge and the recently induced groundwater flow at Tanllwyth.*

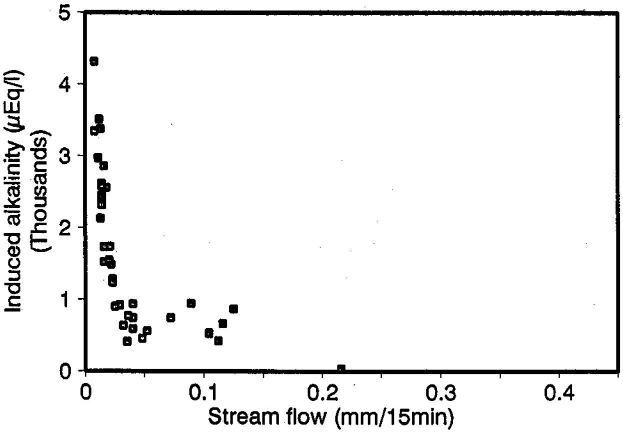

Fig. 9 *The computed change in recently induced groundwater Gran alkalinity at Tanllwyth.*

at peak flow during the event of 18th July 1995, the concentration of calcium at 4.6 mg l^{-1} in the Tanllwyth was nearly 4 times greater than that in the Hafren (Table 4).

For this study, stream water samples were collected from a turbulent well mixed part of the stream channel. 'Dead zone' areas at the channel margin where water exchange with the main flow is relatively slow (Reynolds *et al.* 1991) allow more calcium-rich water to persist even at moderately high flows, thereby providing a refuge for fish and invertebrates. Such 'dead zones' have been noted in studies on lowland rivers. However, similar but smaller zones may exist in upland streams, the size of the Hafren and Tanllwyth, where areas of undercut bank, boulders and fallen trees provide suitable obstructions. Preliminary findings from the nearby afforested Cwm catchment provides some support for this hypothesis; anomalously rich invertebrate fauna have been observed at tributary sites associated with highly alkaline stream water chemistry in an otherwise impoverished, acidic catchment (Hudson *et al.* 1996). The atypical chemical and temperature conditions at these sites are considered to be indicative of groundwater inputs.

Water quality conditions within stream bed gravels are important for fish egg survival (Harriman et al 1990). Groundwater enters the Tanllwyth via the stream bed. Provided the stream sediments are relatively stable and there is slow mixing of interstitial gravel and stream channel water, intra-gravel water chemistry in the vicinity of the seepage may remain relatively alkaline even under high flow conditions. This would favour the survival of fish eggs and bottom dwelling invertebrates. However, the deposition of iron in the vicinity of the borehole seepage may counteract the beneficial effects of increased calcium concentrations and alkalinity.

Table 4. Stream chemistry at storm flow peak in the Tanllwyth and Hafren on 18th July 1995.

	Tanllwyth	Hafren
pH	4.25	4.52
Ca (mgl^{-1})	4.60	1.24
Al (mgl^{-1})	0.50	0.33

For the Tanllwyth, it remains uncertain whether or not the water quality changes will improve the biological status of the stream. Clearly, at the highest flow levels, acid surges will still occur and acute or chronic effects may well be important. For the Plynlimon area, water quality improvements have been observed for the most acidic stream and it is reasonable to assume that, for less acidic steams, the improvements would be greater in response to similarly alkaline base-rich groundwater inputs.

Presently, regional water quality catchment management plans are being developed throughout Wales and England (eg, NRA, 1995). For the upland areas examined within these plans, the problems of stream acidity and impoverished biological status have been identified as of major concern and many streams have been designated for improvement. As most of these areas are underlain by hard rocks similar to those at Plynlimon, there may be potential for groundwater manipulation where groundwater tables are above the stream and regional rock fracturing is suitably aligned. There remain many questions over the distribution of fracturing and regional hydrogeological controls (Banks and Banks, 1993; Neal *et al.*, 1997) but clearly groundwater flow routes are very important to stream-flow generation and water quality in hard rock areas such as Plynlimon (Neal *et al.*, 1997). Future work should thus be directed to examine whether stream water quality improvement using groundwater resources is a practical possibility at a regional level.

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