



The occurrence of groundwater in the Lower Palaeozoic rocks of upland Central Wales

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Abstract

A series of boreholes of up to 50 m depth, drilled into Lower Palaeozoic mudstone, shale and greywacke bedrock in the headwater catchment areas of the River Severn at Plynlimon in Central Wales, shows an extensive chemically- and hydrologically-active shallow groundwater fracture flow system. Groundwater chemistry varies in space and time with lowest water levels and highest alkalinities occurring during the drier summer months. The groundwaters are enriched in base cations, silica, sulphate and alkalinity relative to surface waters indicating significant silicate weathering sources and sulphide oxidation. These sources provide important contributions to both stream water quality and flow. At one site, the introduction of a borehole near to the main river opened bedrock fractures which increased the amount of groundwater entering the river. This had a profound effect on the river water quality by increasing the pH, alkalinity and calcium concentrations. As well as pointing to the possibility of the wider availability of groundwater resources in upland areas, the results highlight (a) the potential value of groundwater as an acid neutralizing resource, (b) the importance of weathering processes and flow routing within the groundwater environment for stream water chemistry, (c) the potential for altering stream water quality by manipulation of groundwater routing and (d) the need to include groundwater characteristics in hydrochemical management models of surface water acidification.

Introduction

Upland areas of hard rock geology, comprising mainly igneous and metamorphic rock of Lower Palaeozoic and Proterozoic age, are extensive across Europe and North America. They represent about 35% of the total European land area and they contribute about 50% of the total surface continental runoff. Soils are often thin with low buffering capacity and the dynamics of water flow are characterised by short residence times; this has major implications for hydrology and water quality. Thus, water in hard-rock terrains is vulnerable to climatic and land use change affecting ecological factors within areas which are often of outstanding natural beauty.

Hard rock areas of upland Wales, as elsewhere in Europe and North America, are at risk to acidification (Hornung *et al.*, 1990; Edmunds and Kinniburgh, 1991), largely because of the slow weathering reactions of silicate minerals (Paces, 1983; Sverdrup and Warfvinge, 1988; White and Brantley, 1995). Neutralization of acidic inputs in these areas occurs by reaction with soil and

bedrock through silicate hydrolysis reactions. Groundwaters are often neutral-to-alkaline even in areas experiencing catchment acidification from acidic deposition and, even in small volumes, may form a major component of stream baseflow which buffers the effects of acidification in streams and lakes.

There is a small but growing awareness that significant volumes of groundwater may be stored in hard rock fracture systems (Edmunds and Savage, 1986): physical evidence includes the sustainment of flows even during the severest of droughts, relatively uniform stream water temperatures throughout the year (Kirby *et al.*, 1991) and variations in soil water storage capacity which are generally much smaller than the variations in catchment water balances (Hudson, 1988).

Over the last decade, hydrogeochemical research in hard rock areas across Europe and North America has highlighted the relative importance of groundwater inputs to streamflow. Rainfall, surface-runoff and the soil-water components tend to be acidic and the groundwater

end-members are less acidic and more highly mineralised; chemical hydrograph separation techniques indicate that there must be a significant volumetric contribution from groundwaters to stormflow runoff (Kennedy *et al.*, 1986; Christophersen *et al.*, 1990; Hooper *et al.*, 1990; Neal *et al.*, 1990a,b). Even quite large streams exhibit an important groundwater input during baseflow as shown by the distinctive bedrock signatures in the groundwater chemistry (Bricker and Rice, 1989; Hornung *et al.*, 1990; Edmunds and Key, 1996; Edmunds and Savage, 1991). One of the uncertainties during hydrograph separation is the relative contribution of soil water and groundwater within the catchment (Christophersen and Neal, 1990). Further awareness and quantification of this process is important as it influences water potability directly; indirectly, it determines the ecology of individual streams.

Isotope hydrology has shown, world wide, that much of the water entering streams during periods of high rainfall has been in soil and shallow groundwater storage and so has the isotopic signature of previous rainfall events (Sklash and Farvolden, 1979; Rohde, 1981; DeWalle *et al.*, 1988; Bonnell *et al.*, 1990; Neal *et al.*, 1992a, 1996; Durand *et al.*, 1993). Consequently, there is a need (a) to improve understanding of the nature of groundwater flow in hard rock environments and (b) to relate groundwater signatures to the interactions with both the soil zone and surface water under different geological and climatic conditions.

This paper presents new findings on groundwater chemistry for intensively monitored hydrochemical upland sites at Plynlimon in central Wales, an area probably characteristic of many hard rock areas comprising low grade metamorphic rocks. Such work is particularly important for the UK as around 30% of the land area is underlain by hard rock; from such terrain possibly 50% of the total UK water supply is derived (cf. DoE, 1995). These areas, mainly in Scotland, Northern Ireland, Wales and northern and southwest England, are typified by low population density and high precipitation; the main economic activities include pastoral farming, forestry and recreation. These areas are also susceptible to ecological damage due to atmospheric deposition of acidic oxides and land use change (UKAWRG, 1988).

This study shows that (a) groundwater resources in hard rock areas are probably more important to stream water quality and quantity than is commonly believed and (b) hard rock aquifers may provide, by manipulation, a means of reducing ecological stress to acidified streams.

Geology, soils, hydrology of the Plynlimon catchments

The study is centred on two sub-catchments which form the main head water drainage areas of the River Severn in mid-Wales: the Afon Hafren (with the Nant Tanllwyth

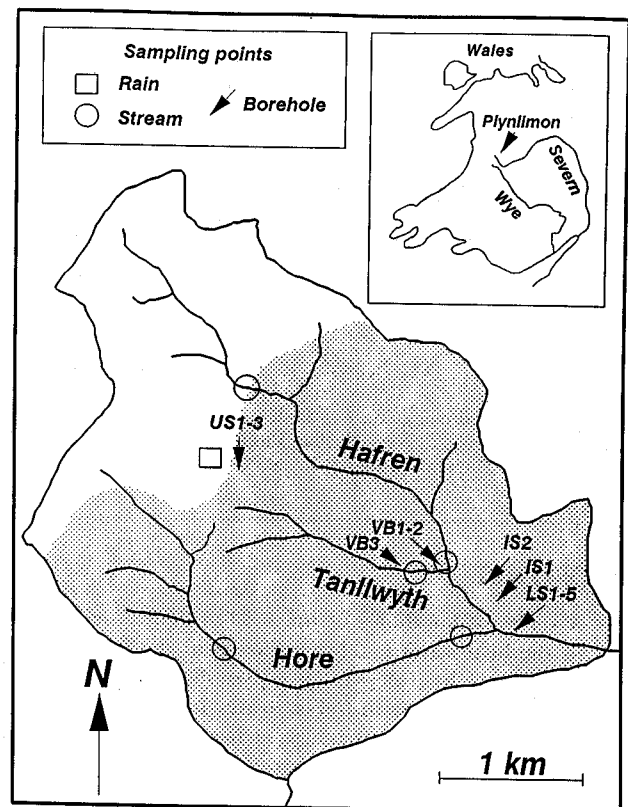


Fig. 1. The Plynlimon study area

tributary) and the Afon Hore (Neal *et al.*, 1990a,b, 1992b,c; Fig. 1; Table 1). Rainfall averages about 2500 mm yr⁻¹, typical evapotranspirational losses amount to around 500–700 mm yr⁻¹ depending on the extent of tree cover. The sub-catchments are of similar altitude range (360–470 m) and size and the storm flow responses are generally rapid and 'flashy'; both have flows which vary between 0.01 and 4.5 m³s⁻¹ (Newson, 1976; Kirkby *et al.*, 1991).

Throughout the sub-catchments, bedrock geology consists of gently folded and low-grade metamorphosed Lower Palaeozoic (Ordovician and Silurian) mudstones, shales and greywackes with a strongly developed high-

Table 1. Catchment details of streams sampled: * indicates catchment fully felled during the sampling period.

Catchment	Area (ha)	% forest (remainder, peat and acid moorland)	Altitude range (m a.s.l)
Afon Hafren	347	52	350–690
Tanllwyth	97	100	350–620
Afon Hore*	335	78	339–738
Upper Hore*	178	56	405–736

angle cleavage. The mineralogy of the mudstones and shales comprises mainly an iron magnesium chlorite, a dioctahedral mica (illite) and quartz with lesser amounts of sodic feldspar pyrite and iron oxides (Hornung *et al.*, 1986; Breward, 1990). The greywacke contains quartz with plagioclase, potassium feldspar, sericite, and chlorite with minor interstitial calcite. The bedrock also contains localized veins containing calcite and Pb-Zn ores. These veins occur mainly within the Hore catchment where several disused adits date from the time Pb-Zn ores were mined. However, the full distribution of vein deposits has not been mapped across the area. The bedrock is covered by a thin soil, typically 70 cm thick, with organic-rich 'L' and 'O' horizons (3 to 10 cm). The lower soils consist of a leached 'E' horizon (10 to 20 cm) and a fine textured podzolic 'B' horizon (about 40 cm thick) merging into a stone 'C' horizon. The predominant soil is a stagno-podzol but peat, brown earth and stagno-gley soils also occur within the sub-catchments.

Acid grassland is dominant in the headwater areas of the Hafren and Hore; on the lower parts, plantation forestry (predominantly Sitka spruce, *Picea sitchensis*) was introduced in various phases between 1937 and 1964 onto acid moorland. The Tanllwyth, originally acid moorland, was afforested completely at the same time as the rest of the Hafren and Hore catchments. Clear-cut harvesting took place on the lower half of the Hore catchment between 1985 and 1989 (Neal *et al.*, 1992*b,c*). The Hafren and Tanllwyth are currently undergoing staged felling and replanting.

Methods

This study relates mainly to work undertaken since the drilling of boreholes in 1993. It builds on an established hydrochemical monitoring programme under which rain and stream waters have been sampled weekly since 1983 and analysed for a wide range of major, minor and trace elements (cf Neal *et al.*, 1990*b*). Summaries of the chemical composition of atmospheric inputs and stream water quality are presented in Tables 2 and 3.

Networks of 11 shallow boreholes (up to 15m depth) and three deep boreholes (up to 50m depth and about 45 m below the river level) were installed within the Hafren (Fig. 1). The Hore was not monitored owing to the much more heterogeneous nature of the bedrock: a much more extensive borehole network was required and this was not practical. The shallow boreholes were drilled at a range of elevations and distances from the Afon Hafren and Nant Tanllwyth while the deep boreholes were drilled near to these rivers. Four broad locations were used.

1) *upper slopes (US)*. Three shallow boreholes were drilled (US1-3) on a 60 m down gradient transect near the edge of the forest on the Plynlimon plateau.

Table 2. Flow weighted means and ranges for rainfall, and Afon Hafren and Afon Hore (pre-felling) stream water. All concentrations are given in mg l⁻¹ (as element or species listed) except for alkalinity (µEq l⁻¹) and pH. Concentration detection limits are all <0.005 mg l⁻¹.

	Rainfall	Hafren	Hore
Na	2.6 (0-24)	3.9 (2.3-5.7)	4.3 (3.0-5.1)
K	0.13 (0-0.9)	0.2 (0.1-1.0)	0.2 (0.1-0.6)
Ca	0.2 (0-2)	0.8 (0.3-2.0)	1.3 (0.6-4.2)
Mg	0.3 (0-3)	0.8 (0.3-1.5)	0.9 (0.6-1.5)
SO ₄	1.6 (0-9)	4.4 (2-12)	5.3 (3-11)
Si	0.34 (0-20)	1.3 (0.5-4.6)	1.5 (1-5.6)
DOC	0.4 (0-3)	1.8 (0-4.4)	1.5 (0-5.6)
NO ₃	0.8 (0-75)	1.5 (0-6)	1.6 (0.4-3.3)
NH ₄	0.3 (0-5)	0.02 (0-1)	0.04 (0-0.8)
PO ₄	0.04 (0-2)	0.05 (0-1)	0.06 (0-0.02)
F	0.03 (0-0.23)	0.05 (0-0.2)	0.05 (0-0.2)
Cl	5.1 (0-44)	7.3 (4-12)	8.24 (5-19)
pH	4.79 (3.4-7.7)	4.46 (4.1-6.8)	4.84 (4.3-7.4)
Alk _{Granl}	-6.7 (-437-201)	-22 (-63-69)	-0.8 (-47-197)

A fault occurred between the top borehole US1 in more permeable grits and the lower boreholes (US2 and US3) in less permeable mudstones.

- 2) *the steep intermediate slopes (IS)*. Two shallow boreholes were drilled (IS1-2), in mudstones and shale, alongside a forest road about 150m from the Afon Hafren.
- 3) *the lower slopes (LS)*. Boreholes LS1 to LS5 were drilled in mudstone and shale bedrock near the Afon Hafren, at distances about 20 m (LS1) to 120 m (LS5) from the stream. Of the shallow boreholes, LS5 was used simply to measure groundwater levels continuously. The deep borehole LS6 was located next to LS1.
- 4) *the valley bottom (VB)*. A shallow (VB1) and a deep (VB2) borehole were drilled near to each other within 100 m of the confluence of the Hafren and the Tanllwyth. These boreholes were established in alluvial gravels consisting of mudstone, shale and greywacke. A further deep borehole (VB3) was located near to the Nant Tanllwyth in mudstone and shale.

Table 3. Major ion chemistries for baseflow and stormflow waters of the Afon Hafren and the upper and lower stretches of the Afon Hore for the period September 1984 to October 1990. All units are mg l^{-1} (as element or species listed) except for alkalinity ($\mu\text{Eq l}^{-1}$) and pH. High flow and low flow correspond with values greater than 0.1 mm/15min and less than 0.01 mm/15 min. Concentration detection limits are all $< 0.005 \text{ mg l}^{-1}$.

Element	Afon Hafren		Upper Afon Hore		Lower Afon Hore	
	Base flow	Storm flow	Base flow	Storm flow	Base flow	Storm flow
Na	3.9	3.9	3.8	4.2	4.2	4.1
K	0.1	0.2	0.1	0.1	0.2	0.3
Ca	1.0	0.8	3.1	0.7	3.1	1.0
Mg	0.8	0.8	0.9	0.4	1.2	0.8
Total Al	0.1	0.4	0.1	0.5	0.1	0.5
DOC	0.8	2.2	1.0	2.0	1.0	1.9
Cl	6.8	7.2	7.0	8.7	7.5	7.9
SO ₄	3.5	4.7	3.1	4.1	4.8	5.1
NO ₃	0.8	1.7	0.8	1.2	1.2	2.5
Alk _{Gran1}	24.2	-28.3	145.7	-27.7	126.6	-16.0
pH	6.3	4.6	7.1	4.6	7.1	4.8

The shallow borehole drilling was undertaken with a top drive hydraulic rotary drilling rig using a rock-roller bit down to bedrock and a down-hole hammer within the bedrock. Both techniques used a 250 cfm/100 psi or 400 cfm/170 psi compressor for flushing rock debris. The overburden was cased off in steel during drilling and the shallow boreholes were lined with nominal 50 mm PVC casing with the bottom section (1–2 m) screened at 0.5 mm slot size. A 1–2 mm graded silica sand pack was emplaced around the well screen and most of the casing. The top 1–2 m was sealed with bentonite pellets to prevent downward leakage from the surface and soil layers. The boreholes were subsequently developed by air lifting. The deeper boreholes were completed open hole, 89 mm diameter and equipped with a short (< 5 m) length of steel casing from the surface.

The networks of shallow boreholes (excluding the water level monitoring site LS5) were sampled monthly for a year, beginning in April 1994, using an open-ended down-hole bailer. For about 2 to 4 months prior to monitoring, the boreholes were bailed regularly to eliminate water quality contamination from rock fines and disturbed rock surfaces associated with the drilling process. Before a water sample was collected for analysis, five or more bailed samples were used to rinse the sample bottle. This ensured that the bottles were not contaminated and that the water collected for analysis had not been standing long within the borehole prior to collec-

tion. The samples were collected in de-ionized-water washed 1 litre glass bottles. On return to the laboratory, sub-samples were taken for (a) immediate pH and Gran alkalinity determination and (b) 0.45 μm filtration, storage in polypropylene bottles at 4°C in the dark to avoid sample deterioration, and subsequent analysis for a range of major and trace components. The deeper boreholes were sampled during pumping, at a range of depths, following geophysical logging.

A combination electrode particularly suited to low ionic strength waters (Radiometer Ltd, electrode GK2401c) was used for the pH measurements. Care was taken to minimise CO₂ degassing (which may increase pH significantly for these waters) by (a) completely filling the bottles and capping firmly, (b) keeping the samples and pH electrodes at groundwater temperatures and (c) analysing samples as soon as possible on return to the field laboratory (usually within one hour of sampling). For Gran alkalinity determinations, an acidimetric titration (Neal and Hill, 1994) was used over two pH ranges 4.0–4.5 (Alk_{Gran1}) and 3.0–4.0 (Alk_{Gran2}): Alk_{Gran1} reflects essentially the bicarbonate buffering (minus the hydrogen ion concentration) whilst Alk_{Gran2} contains an additional term for organic acid buffering. The analytical procedures for the other determinands included inductively coupled plasma optical emission spectroscopy for the major cations, atomic absorption for potassium and automated colourimetry for the major anions and silica.

Results

A) GROUNDWATER HYDROLOGY

Groundwater was found at all the drilling sites. Typically, the water table was about 5 m below ground level but depths varied both in space and time (Table 4, Fig. 2). None of the boreholes dried up during the summer months and all but the shallowest boreholes showed rapid response to rainfall, with levels varying by up to 4 metres. Two of the boreholes (LS2, VB3) were artesian during most of the winter months.

The deeper boreholes (VB2, VB3 and LS6) were logged geophysically using the BGS Wallingford logger. A suite of formation log measurements including calliper, gamma ray, focused and induction resistivity, neutron porosity, density and magnetic susceptibility was run to characterise the formations. Fluid logs (fluid electrical conductivity, fluid temperature and borehole flowmeter) were run to identify horizons with active groundwater flow.

Fluid log measurements, made in the unpumped boreholes and repeated whilst pumping, allowed inflows to be identified and their relative contribution to total yield determined in relation to the geology. In one case, (LS6), 80% of the total yield was obtained below 30 m depth (Fig. 3); at high yielding VB3 ($Q/s = 461$ l/min/m) 75% was obtained above 11m and 25% from 32–33m

depth (Fig. 4). The specific capacities for the three deep boreholes, as determined from water level measurements made during short periods of pumping (100 minutes), were 7.9, 14 and 461 l/min/m. Conventional correlation matching of the formation and water-bearing horizons between the boreholes could not be undertaken because of the high dip of the strata. The unstressed groundwater temperature logs indicated a local base of groundwater circulation at 32–33 m depth; water was markedly cooler above approximately 10 m depth in the three deep boreholes. This implies that shallow groundwater storage and circulation is probably important in the catchments.

B) GROUNDWATER CHEMISTRY

Relative to the stream, most of the groundwaters were of high alkalinity, indicating significant water-rock interaction (Table 4): values of pH of these waters ranged from 7 to over 8, after allowing for the effects of degassing to atmospheric pressure. The groundwater chemistry spans the range observed within the stream during low flow conditions (cf Tables 3 and 4). However, there is a large range in the groundwater hydrochemistry and, in a few cases, pH, alkalinity and base cation concentrations are much higher than those observed in the stream (Tables 3 and 4).

Table 4a: The chemistry of the exploratory boreholes. All units are mg l^{-1} (as element or species listed) except alkalinity ($\mu\text{Eq l}^{-1}$), depth (m) and pH. Concentration detection limits are all <0.005 mg l^{-1} .

	US1			US2			US3		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
pH	4.95	4.69	5.83	5.38	5.13	6.43	5.16	5.05	5.41
alk1	28.50	-2.71	77.58	30.42	10.71	72.00	25.74	7.89	49.63
alk2	28.64	0.00	86.92	12.71	0.00	32.44	15.78	0.00	41.22
depth	0.89	0.56	1.95	11.58	8.66	14.36	9.96	7.36	12.77
Cl	8.12	5.40	11.80	10.20	8.40	11.20	7.05	5.70	8.20
NO3	0.07	0.00	0.40	1.33	0.71	1.50	1.23	0.93	1.59
NH4	0.02	0.00	0.04	0.04	0.00	0.22	0.03	0.00	0.09
Na	5.62	4.60	7.20	6.10	5.50	6.40	4.03	3.50	4.80
Mg	0.61	0.30	0.70	0.78	0.70	0.80	0.65	0.60	0.70
Ca	0.93	0.56	1.51	1.10	0.76	1.91	1.11	0.89	1.41
SO4	4.08	3.10	5.20	3.15	2.40	5.00	2.54	2.30	2.80
Sr	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Mn	0.07	0.03	0.10	0.08	0.03	0.23	0.05	0.03	0.10
Fe	0.08	0.00	0.20	0.05	0.00	0.48	0.03	0.00	0.29
Zn	0.08	0.03	0.26	0.06	0.03	0.18	0.07	0.00	0.22
Al	0.29	0.00	0.49	0.01	0.00	0.12	0.01	0.00	0.10
Si	1.18	0.70	2.20	2.15	1.70	3.00	1.78	1.25	5.10
EpCO2	78.2	14.0	159.4	23.1	4.2	32.9	36.1	20.1	56.0
pH degas	6.20	5.29	6.79	6.33	5.97	6.76	6.29	5.87	6.60

Table 4b: The chemistry of the exploratory boreholes. All units are mg l^{-1} (as element or species listed) except alkalinity ($\mu\text{Eq l}^{-1}$), depth (m) and pH (dimensionless). Concentration detection limits are all $<0.005 \text{ mg l}^{-1}$.

	LS1			LS2			LS3			LS4		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
pH	4.6	4.3	5.8	5.7	5.1	6.2	5.2	4.9	6.6	5.4	4.7	6.4
Alk _{Gran1}	-20.0	-30.0	35.2	141.0	19.0	887.0	50.0	3.2	466.0	87.0	-10.0	407.0
Alk _{Gran2}	-6.2	-20.0	47.0	70.0	0.0	192.0	15.0	0.0	94.0	50.0	-5.0	404.0
depth	2.29	1.19	12.9	0.61	0.0	1.7	1.7	0.1	3.3	4.7	1.8	5.9
Cl	10.4	7.6	12.0	11.4	10.6	12.4	11.4	10.4	12.6	11.5	9.90	13.4
NO ₃	0.84	0.40	1.28	0.77	0.40	1.05	1.0	0.71	1.27	0.64	0.0	1.0
NH ₄	0.02	0.0	0.06	0.06	0.01	0.15	0.03	0.0	0.06	0.04	0.0	0.11
Na	6.58	4.40	7.30	7.15	6.0	7.60	6.99	6.10	7.40	7.81	7.03	8.90
Mg	1.45	0.70	1.70	1.50	1.20	1.70	1.61	1.10	4.20	2.05	1.29	4.10
Ca	1.80	1.13	2.04	1.74	1.26	2.22	2.16	1.10	9.47	3.67	1.28	9.49
SO ₄	12.7	2.70	15.6	8.83	6.40	10.3	8.4	6.40	14.6	13.5	7.2	24.3
Sr	0.02	0.01	0.11	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02
Mn	0.05	0.04	0.07	0.14	0.04	0.26	0.08	0.02	0.66	0.12	0.03	0.33
Fe	0.12	0.0	0.76	1.28	0.0	2.71	0.01	0.0	0.06	0.12	0.0	0.89
Zn	0.06	0.03	0.23	0.01	0.0	0.04	0.07	0.0	0.27	0.03	0.0	0.11
Al	0.48	0.0	0.68	0.0	0.0	0.0	0.06	0.0	0.19	0.03	0.0	0.14
Si	2.32	1.80	2.75	1.90	1.40	2.75	2.11	1.75	2.45	2.82	1.50	4.80
EpCO ₂	24.0	—	166.0	36.0	6.0	241.0	25.0	17.0	57.0	26.0	16.0	44.0
pH degas	4.7	4.5	6.4	6.8	6.2	7.8	6.2	5.6	7.5	6.3	4.9	7.5

Table 4c: The chemistry of the exploratory boreholes. All units are mg l^{-1} (as element or species listed) except alkalinity ($\mu\text{Eq l}^{-1}$), depth (m) and pH. Concentration detection limits are all $<0.05 \text{ mg l}^{-1}$.

	IS1			IS2			VBI		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
pH	5.35	5.05	5.49	5.47	4.77	5.79	5.87	5.16	6.82
Alk _{Gran1}	20.51	6.81	30.67	63.93	11.98	166.24	1304.82	41.14	4953.0
Alk _{Gran2}	14.96	0.0	41.43	35.12	0.0	163.22	332.02	0.0	3966.20
depth	8.09	5.89	9.53	6.11	3.31	7.20	1.88	1.10	2.52
Cl	10.72	8.60	12.20	12.04	11.0	14.0	5.29	4.60	6.10
NO ₃	0.71	0.58	0.84	0.63	0.20	0.93	0.79	0.0	2.17
NH ₄	0.06	0.0	0.16	0.04	0.0	0.11	0.08	0.01	0.19
Na	6.60	5.70	7.10	7.26	6.30	8.30	5.96	3.20	13.60
Mg	1.29	1.0	1.50	1.83	1.10	3.20	5.67	0.70	18.80
Ca	1.96	1.43	2.47	5.25	2.52	9.12	16.08	1.34	55.0
SO ₄	8.06	6.30	9.90	15.89	8.70	28.0	3.73	3.10	5.0
Sr	0.01	0.01	0.01	0.01	0.01	0.03	0.06	0.01	0.23
Mn	0.02	0.02	0.04	0.15	0.05	0.37	0.33	0.13	0.77
Fe	0.0	0.0	0.03	0.13	0.0	1.95	0.74	0.0	3.73
Zn	0.07	0.03	0.14	0.10	0.03	0.26	0.06	0.0	0.26
Al	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Si	1.82	0.08	4.35	3.09	1.35	3.95	3.35	1.85	7.10
EpCO ₂	19.08	10.99	41.09	33.62	16.15	78.69	73.91	34.97	155.95
pH degas	6.21	5.82	6.40	6.60	6.02	7.12	7.40	6.52	8.60

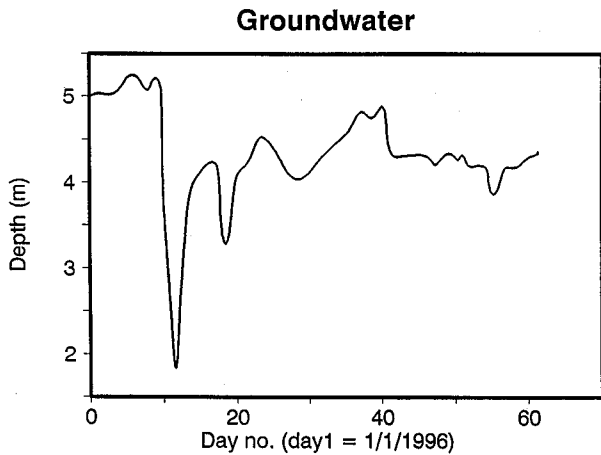


Fig. 2. The water level variations for the LS4 borehole over time for the period January to March 1996.

Cation and anion concentration relationships in groundwaters can characterize parent materials that have undergone weathering. The main inter-relationships are shown in Fig. 5a,b. With the exception of US1 and VB1, sodium is highly correlated with chloride and the Na/Cl ratio is 0.60 compared to 0.51 for sea water and 0.55 for Plynlimon rainfall (on a mg l^{-1} to mg l^{-1} basis). This indicates a predominant maritime source for sodium (about 85% assuming, reasonably, that Cl comes from the atmosphere). Systematic site to site variations in sodium and chloride concentrations are observed with the highest values occurring beneath the forest: ie in areas where there is enhanced atmospheric scavenging of sea salts and greater evapotranspiration. Strong correlations between calcium, magnesium and sulphate are probably indicative of pyrite oxidation and of weathering of calcium and magnesium bearing minerals: sulphide oxidation increases weathering reactions by generating hydrogen ions which on neutralization yield high base cation levels. Gran alkalinity is also highly correlated with pH although the relationship is non-linear. Silica is enriched in the groundwaters with mean concentrations in the range 1.2 to 3.4 mg-Si l^{-1} . These concentrations are approximately at saturation with respect to microcrystalline SiO_2 (Chalcedony; about 3 mg-Si l^{-1} at 8 °C) and are indicative of a source from the weathering of silicate minerals. There appears to be an upper limit to silica solubility which is probably not controlled strictly by equilibrium with silica minerals but may also be limited by adsorption onto silica surfaces (Casey and Neal, 1986). Nitrate concentrations are low ($<2 \text{ mg-NO}_3 \text{ l}^{-1}$) and are at their lowest in forested areas where biochemical demands are at their highest. However, the absence of measurable nitrate in some boreholes suggests that reducing conditions occur. This is supported by the variable concentrations of dissolved iron; concentrations of

iron ($<0.45 \mu\text{m}$) above 0.1 mg l^{-1} probably indicate the presence of iron in its more soluble reduced divalent state (Fe^{2+}). Indeed, for all the boreholes exhibiting nitrate concentrations below the analytical detection level, the waters prior to filtration contain pale yellow/green to brown amorphous flocculates which are probably freshly precipitated iron oxides/hydroxides.

Three of the shallow boreholes differed from the rest of the sites. These were as follows.

a) US1 and LS1.

These boreholes have probably intercepted soil water and near-surface groundwater as the waters are more acidic than those at the other sites and groundwater levels are close to the ground surface. The waters were also enriched in aluminium and seemed more characteristic of soil drainage and soil interstitial solutions than groundwater. For US1, the relationship between sodium and chloride follows two linear lines (Fig. 5a); in autumn, sodium is enhanced relative to chloride with respect to most of the other borehole waters. This indicates an enhanced sodium weathering component during the part of the year where water residence times are high.

b) VB1 which penetrates gravels.

During the first summer of sampling of VB1, high alkalinities were recorded (up to around $5000 \mu\text{Eq l}^{-1}$, 300 mg l^{-1} as HCO_3). In the subsequent winter months, the alkalinity decreased to around $100 \mu\text{Eq l}^{-1}$ and high alkalinities did not recur in the following summer. All the waters were undersaturated with respect to calcite. For example, the logarithm of the saturation index for calcite is in the range -0.6 to -2 at the high alkalinities and less than -1.5 at the low alkalinities. Element relationships differed markedly from the other sites (cf. Figs. 5a and 5b). The only strong correlations observed were between Gran alkalinity, pH, sodium, potassium, calcium, magnesium and silica. Notably, the groundwaters had a high Na/Cl ratio relative to Plynlimon rainfall and sea water (1.13, 0.51 and 0.55, respectively, on a mg l^{-1} to mg l^{-1} basis). This indicates a localised internal source of sodium, probably related to the weathering of albite.

The difference in alkalinities between subsequent summer months is explained by either or a combination of two processes. Firstly, slow kinetic weathering controls within the groundwater fracture system may inhibit re-equilibration within a time span of one year (cf. Sverdrup and Warfvinge, 1988): this high alkalinity store is likely to be of relatively small volume and long residence time. Secondly, there may be a hydrological control, inducing intermittent recharge of shallow low alkalinity water. The lack of correlation between sulphate and the base cations and alkalinity and the low concentrations observed, compared to the other shallow boreholes, is indicative of lesser sulphide oxidation at the VB1 site.

All the deep boreholes have groundwaters with high

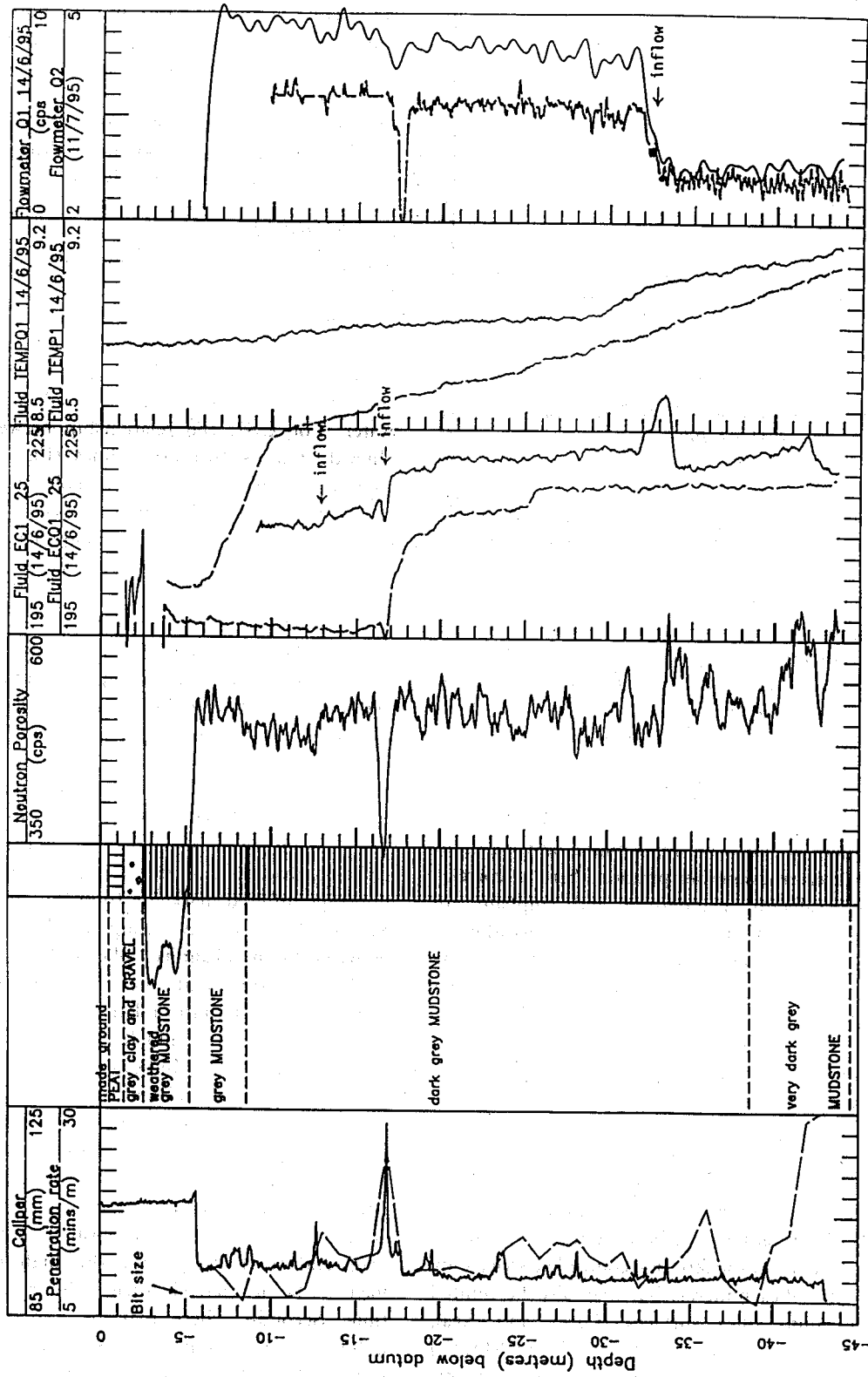


Fig. 3. Deep borehole logs for the LS6 site.

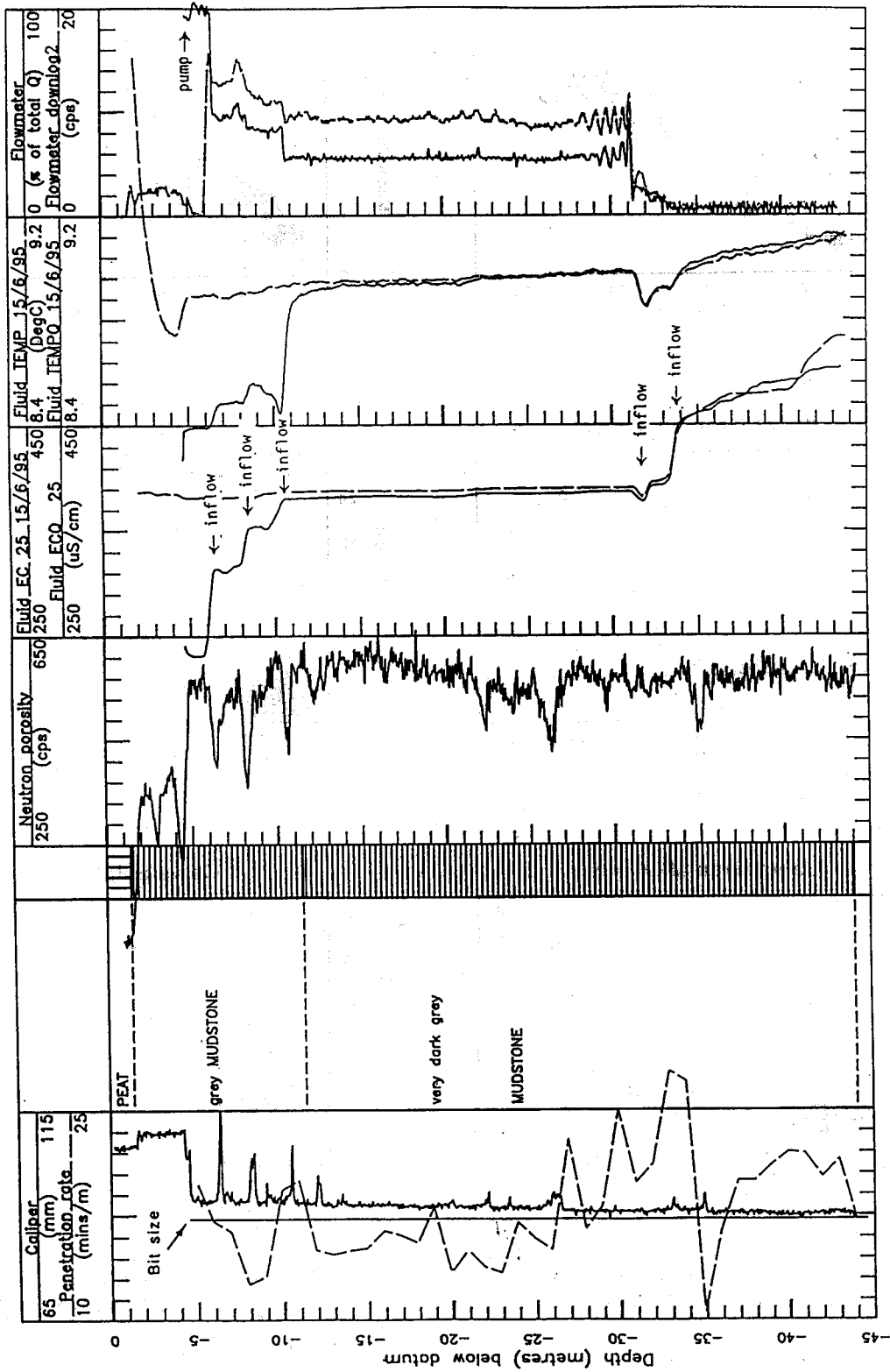


Fig. 4. Deep borehole logs for the VB3 site.

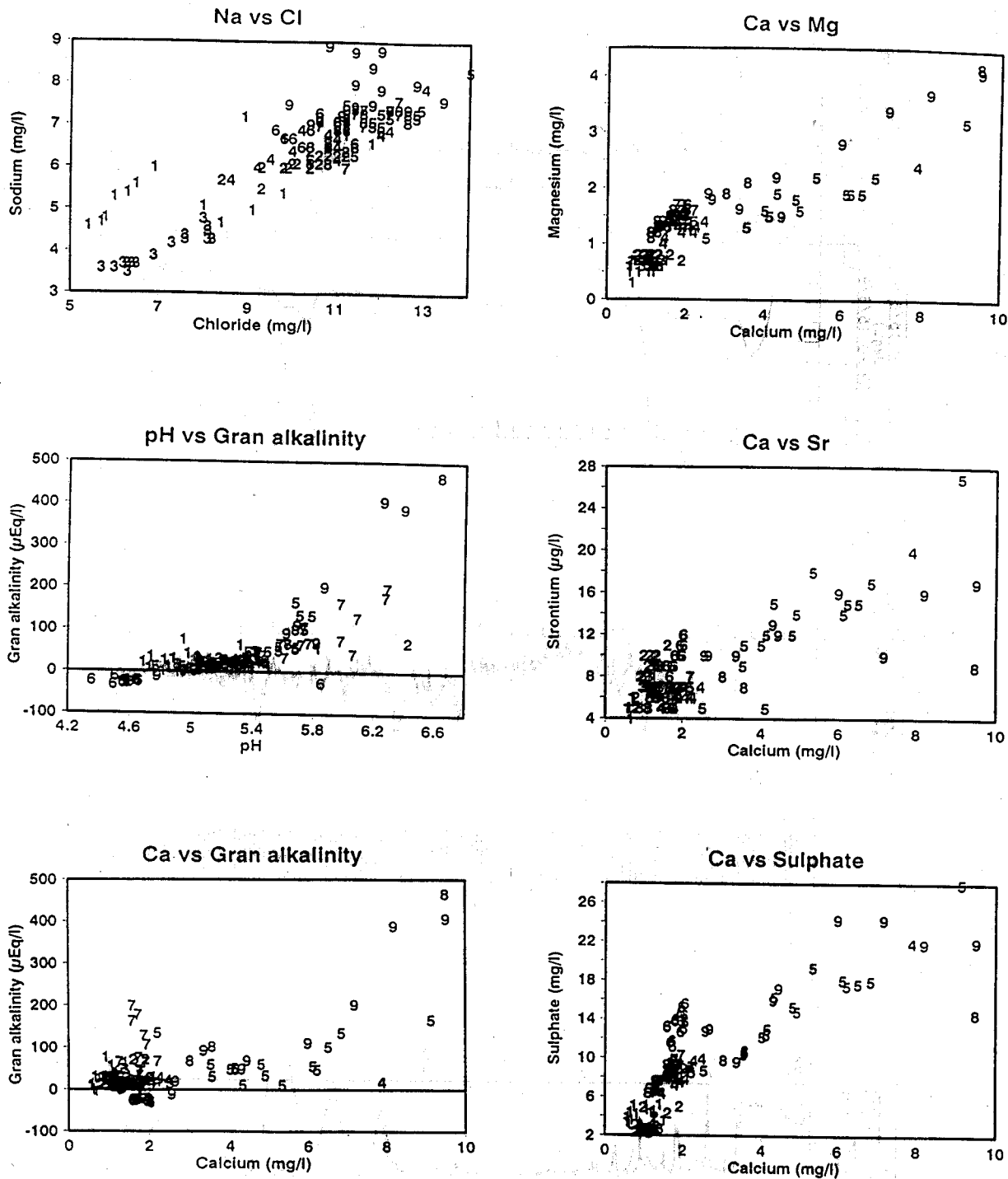


Fig. 5a. Examples of major cation, chloride, sulphate and silica concentration inter-correlations for the exploratory boreholes other than VB1. Within the graphs, each borehole is denoted by US1=1, US2=2, US3=3, IS1=4, IS2=5, LS1=6, LS2=7, LS3=8, LS4=9.

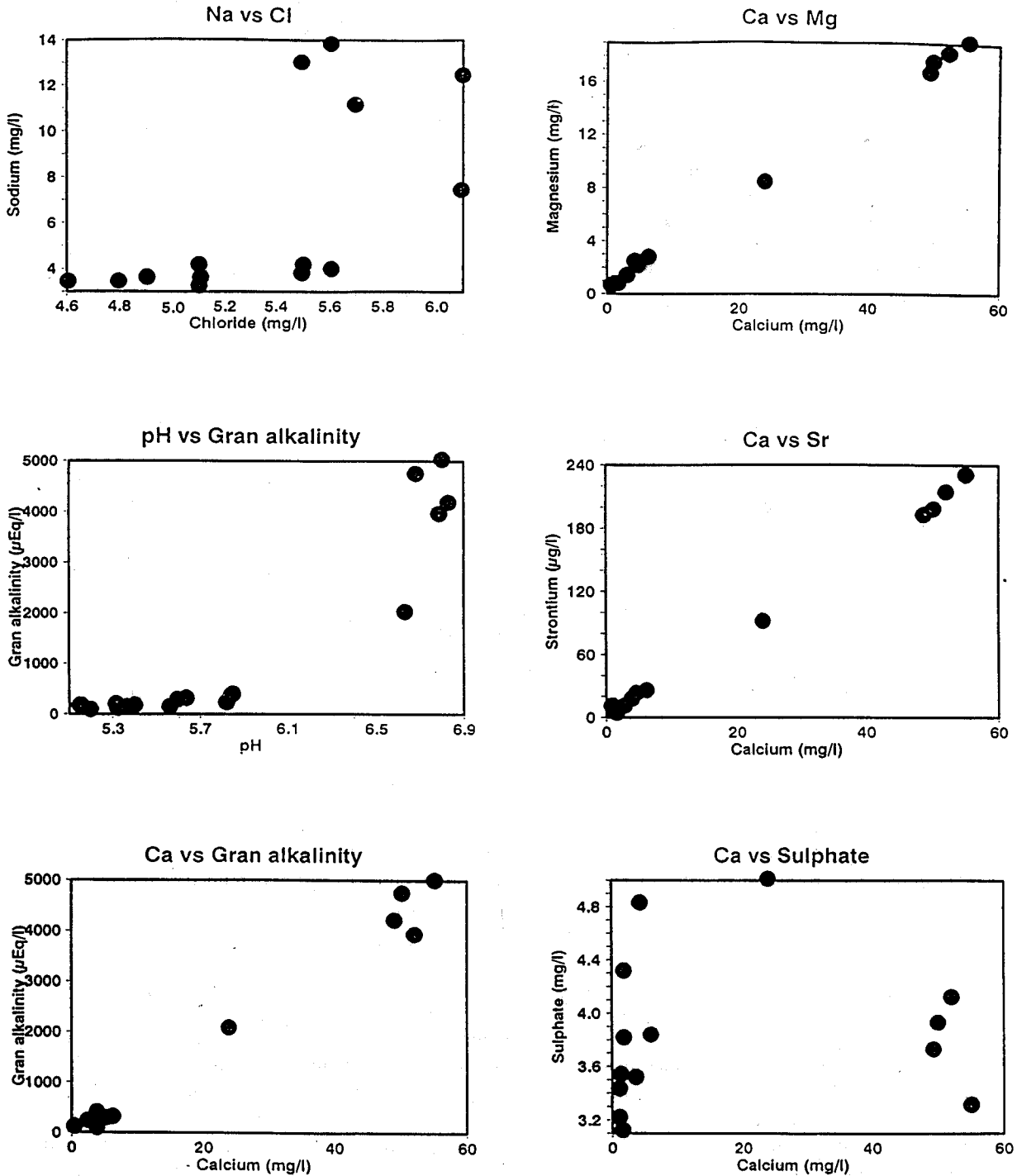


Fig. 5b. Examples of major cation, chloride, sulphate and silica concentration inter-correlations for the exploratory borehole VB1.

alkalinities (Fig. 6). Components associated with weathering (Gran alkalinity, silica and base cation concentrations) are higher than for nearby shallow boreholes, but sulphate concentrations are comparable. A discharge sample collected during pumping of the deep borehole VB2 was dominated by a shallow input containing

significantly lower solute concentrations than those found at depth: logging information indicated a leak at a casing joint at 3m depth with inflow at the base of the shallow casing. The results indicate that there is chemical stratification in the groundwaters with a more chemically evolved water at depth. The main source of base cations

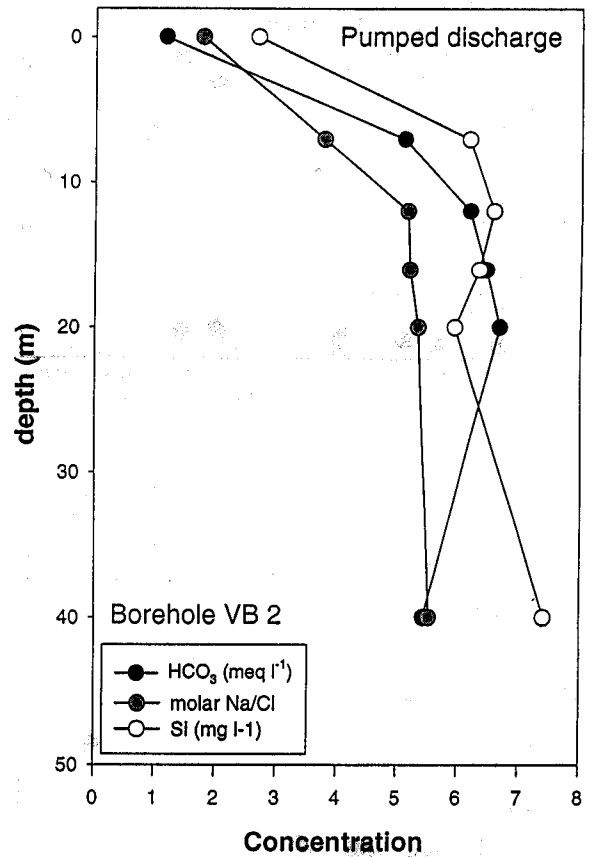
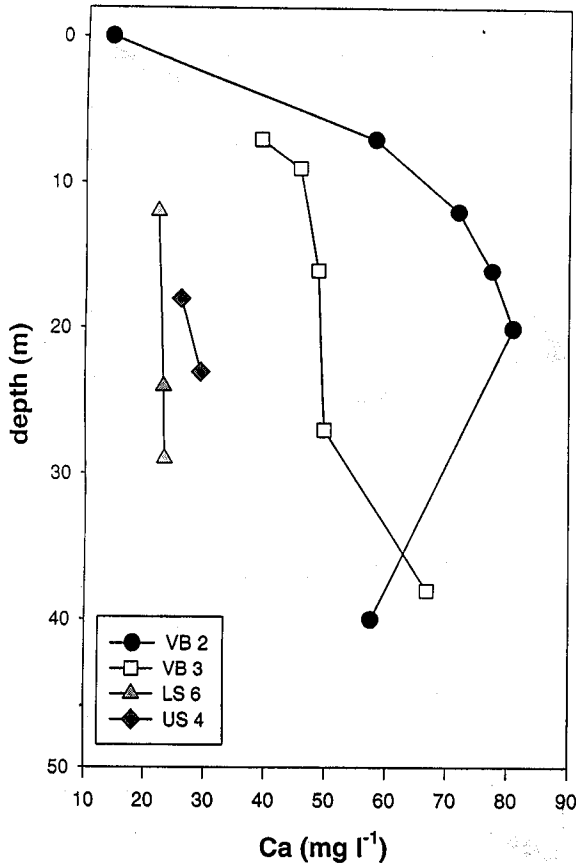


Fig. 6. Alkalinity variations with depth for the deep borehole sites.

and alkalinity in the groundwaters' weathering seems to come from silicates rather than carbonates in the bedrock. For example, the strontium to calcium ratio in the streams is high (about 0.10–0.02) relative to that expected from the congruent dissolution of calcites (<0.00009). Associated isotopic work indicates similar to higher ⁸⁷Sr/⁸⁶Sr ratios in the stream waters compared with calcite (0.7120–0.7148 and 0.7119 respectively; Shand et al., 1996).

During the air-flush drilling of VB3, a fracture route to the stream was opened up. Intensive bubbling was observed from the nearby Tanllwyth stream bed during periods of air flushing. Subsequently, brown precipitates, formed along bedrock fractures in the stream bed, were seen during low flow. Time series of pH and calcium concentrations indicate clearly a major chemical change for Tanllwyth stream waters following the construction of the borehole (Fig. 7). The change persists for low to moderate flows; pH has increased by about 0.5 units (except at very high flows) and baseflow calcium concentrations have increased up to five fold. There is no corresponding change for the Hafren (Neal et al., 1997). A survey along the stream indicated that the abrupt 0.5 pH unit change occurred close to the borehole; this confirms that the local groundwater input was the source of the

change and that the process of drilling and flushing had augmented the transmissivity of the aquifer by removing chemical precipitates and fine grained sediment.

Discussion

The results indicate an extensive and hydrologically active groundwater system within the upland Plynlimon catchments. This groundwater system is dominated by fracture flow movement from the ground surface to 30 m or more below the stream. While the specific capacity of the boreholes can be high, the volume of storage remains unknown. Markedly cooler groundwater temperatures and a higher neutron porosity above 9 m suggest more rapid circulation and greater storage of groundwater at shallow depth. Chemical gradients with depth occur in base cations, silica and Gran alkalinity, probably indicative of increased residence times. Chemical and hydrological variability is large even on a local scale: this reflects the combined effects of variability of flow pathways, residence times and weathering rates. Also, the variability of dissolved iron and nitrate, probably is affected by variability of redox conditions in local domains in the soil/shallow-bedrock environment, enhanced by the presence of organic matter.

The shallow hydraulically-active groundwater component probably supplies the major proportion of groundwater entering the stream: the more chemically reacted groundwater is volumetrically less important and is likely to form part of a deeper water circulation system controlled by faulting at the regional scale. Within the groundwater system, carbonates are rare and the main weathering process involves the breakdown of the Fe-Mg chlorite and the oxidation of pyrite. However, in localised pockets, sodic plagioclase weathering can promote particularly high alkalinities and sodium concentrations in the shallow groundwater. Furthermore, the variations over time in the chemistry and water level for the shallow groundwaters indicate influxes of water from the soil zone. Both the volume and chemistry of these waters will differ according to soil type (peaty gleys,

peaty podzols and brown earths) because these soils have different chemistries and hydrological properties. Thus, the soil type exerts some control over the physical and chemical responses both within the shallow groundwater and the stream.

The Gran alkalinities of all the groundwaters are higher than can be accounted for by neutralization of strong acids in the rain and soil. They relate instead to oversaturation with respect to carbon dioxide. The excess partial pressure of carbon dioxide ($EpCO_2$) is the ratio of the dissolved undissociated inorganic carbon in the water sample divided by the dissolved undissociated inorganic carbon in pure water in equilibrium with the atmosphere (Avila and Roda, 1991; Neal, 1996). It can be approximated by:

$$EpCO_2 = [HCO_3^-] \times [H^+] / 5.25$$

where the bicarbonate and hydrogen ion concentrations are given in units of $\mu Eq l^{-1}$. $EpCO_2$ is calculated using this equation from the pH measurement: bicarbonate concentration is estimated from the Gran alkalinity (ALK_{Gran1}) measurement using (Neal, 1996):

$$[HCO_3^-] = Alk_{Gran1} + [H^+]$$

These equations show that a reduction in $EpCO_2$ following carbon dioxide degassing will be associated with a rise in pH as the Gran alkalinity is conserved chemically.

The $EpCO_2$ estimates of this calculation show that the waters are typically oversaturated with respect to carbon dioxide by 30–100 times the atmospheric value. The high partial pressures mean that groundwater pH will increase substantially when the water degasses to equilibrium with the atmosphere in the stream. The rise in pH on degassing is most marked at high Gran alkalinities (over one pH unit). For example, at the VB1 site, the highest recorded pH before degassing was 6.82; with degassing the calculated pH rose to 8.6. This rise was confirmed by equilibrating a field sample with air—the measured pH for the degassed sample was between 8.5 and 8.65.

The high partial pressures of carbon dioxide reflect either organic carbon decomposition within the soil and groundwater areas or direct CO_2 supplies from deeply penetrating roots. Of the two processes, the former is probably dominant as microbiological processes clearly can operate within soil and groundwater systems to promote CO_2 production from organic carbon breakdown (Chapelle, 1993). Supplies from root systems are likely to be limited since conifer roots are confined mainly to shallow (<1–2m) depth at Plynlimon.

Most catchment weathering studies have concentrated on areas where bedrock mineralogy is relatively simple (typically coarse grained igneous and metamorphic rocks) and where dominant weathering reactions and products are known (Paces, 1983; Sverdrup and Warfvinge, 1988;

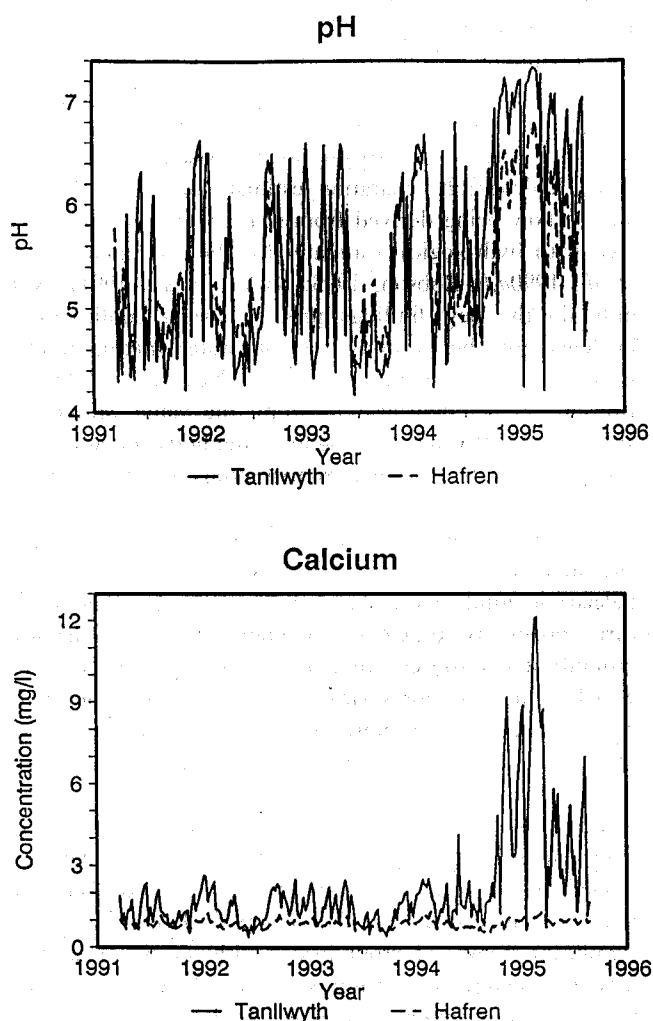


Fig. 7. The variations in pH and calcium concentration with time for the Nant Tanllwyth and Afon Hafren: the deep borehole which subsequently affected Tanllwyth stream water chemistry was introduced in May 1994.

Drever and Clow, 1995; White and Blum, 1995; White and Brantley, 1995). Characterizing the minerals and weathering reactions in catchments dominated by fine grained rocks such as shales and mudstones is extremely difficult. The soil mineralogy at Plynlimon is related to the bedrock mineralogy but alteration of chlorite and transformation of illite to vermiculite take place in the upper parts of the soil. Chlorite is relatively rare in the upper soils but increases with depth; in contrast, vermiculite is more common in the upper parts of the soils (Hornung *et al.*, 1986).

Vein mineralisation and vein calcite weathering is a major control on calcium concentrations for both the Afon Hore (Reynolds *et al.*, 1986) and the Nant Iago stream in the adjacent Wye catchment (Hornung *et al.*, 1986). This weathering of calcite has important effects on the ability of individual catchments to buffer atmospheric acidic inputs. Calcite is conspicuously absent in Plynlimon soils and, apart from vein mineralisation, is rare as a component of the Lower Palaeozoic mudstones of Wales. Calcite dissolution is likely to have occurred in waters draining the Afon Hore. This is indicated by the relatively high calcium and low strontium to calcium ratios (0.0020–0.0025 for the Hore compared with 0.0033–0.0050 for the Hafren) and the degree of calcite undersaturation (typically an order of magnitude or more). However, some calcium must also be derived from silicate weathering.

Preliminary mass balance calculations (Durand *et al.*, 1994) indicate significant losses of base cations and silica from all catchments, whereas the alkali metals sodium and potassium are reasonably well balanced: the input-output balance for sulphate is presently uncertain because unmeasured inputs from occult and dry deposition of SO_x and sulphate may be high. Thus, it seems that weathering of both silicate and carbonate rocks provides important controls on the base cations and silica. Base cation losses are high in comparison with those found in several other studies of catchments on acid metamorphic and igneous rocks, indicating the relatively high reactivity of mudstones and shales. Clearly, this is enhanced to a significant degree where carbonate veins are present in the catchment.

Conclusion

The network of boreholes and the evaluation of the hydrology and hydrochemistry show clearly that an extensive shallow groundwater system occurs in the uplands of mid-Wales associated with fracture flow movement. This system is chemically and hydraulically active and highly heterogeneous in nature. The fractures probably supply not only groundwaters to the stream, but also routes for the transfer of soil water which is then modified by interaction with the bedrock. The groundwaters show increasing mineralisation with depth

and the fact that they are enriched in base cations, sulphate and alkalinity indicates the presence of weathering sources. Clearly, such sources provide the significant contributions of high alkalinity and mineralized groundwater loading to a high river water quality standard.

This study, in association with earlier findings on soils (Robson, 1993), indicates a highly heterogeneous system, both within the soils and the groundwaters. Yet, remarkably, the patterns observed within the stream are relatively simple and an endmember mixing approach at a coarse scale seems suitable for describing the water quality variations occurring in the river during a storm. Within environmental studies, it is usual to lump the heterogeneity in providing predictive models for environmental impact assessment and remedial treatment. However, this lumping procedure may be inappropriate because different parts of the catchment are responding in different ways (Christophersen and Neal, 1990; Neal, 1996). None the less, the study confirms, in general terms, the findings of the hydrograph separation studies for Plynlimon using the measured acid neutralizing capacity (ANC). For example, the pHs and alkalinities in the groundwaters are high enough to explain values observed within the stream during baseflow. Also, the ANC hydrograph separation estimate of about 25% of stream flow being derived from shallow groundwaters fits well with hydrological estimates for the catchment (Neal *et al.*, 1990*a,b*; Robson, 1993; Kirkby *et al.*, 1991). Not only do the new findings provide strong confirmatory evidence for the groundwater–soil water mixing model hypothesised for Plynlimon streams (Neal *et al.*, 1990*a,b*; Robson, 1993); they also illustrate the value, simplicity and cost effectiveness of chemical methods for assessing physical aspects of water contributions to stream flow generation.

The Plynlimon area is typical of many areas of upland Britain and wider afield which are underlain by Lower Palaeozoic mudstones, shales and greywacke. The fracture porosity is sufficient to contain widespread shallow groundwater resources to a depth of 30 m; these may well be important for sustaining water supplies for small communities. Furthermore, weathering reactions in the saturated zone influence stream water chemistry significantly.

These findings have wide implications for catchment management because of the normal, but here demonstrated to be incorrect, assumption that such bedrock types are impermeable and unreactive. The presence of significant storage of groundwater with positive alkalinity may well neutralize acid inputs from atmospheric deposition and afforestation; experience in the Tanllwyth suggests groundwater manipulation may also provide a means for reversing stream acidification as proposed for upland areas of Scotland and Wales (Cook *et al.*, 1991; Neal *et al.*, 1997). Thus, the groundwater hydrogeochemical processes described here are of fundamental

importance to the modelling of acidic deposition and land use change and environmental water quality management in these regions of environmental stress.

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