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Acid neutralization capacity measurements in surface and ground waters in the Upper River Severn, Plynlimon: from hydrograph splitting to water flow pathways

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Abstract

Acid Neutralization Capacity (ANC) data for ephemeral stream and shallow groundwater for the catchments of the upper River Severn show a highly heterogeneous system of within-catchment water flow pathways and chemical weathering on scales of less than 100m. Ephemeral streams draining permeable soils seem to be supplied mainly from shallow groundwater sources. For these streams, large systematic differences in pH and alkalinity occur due to the variability of the groundwater sources and variability in water residence times. However, the variability cannot be gauged on the basis of broad based physical information collected in the field as geology, catchment gradients and forest structure are very similar. In contrast, ephemeral streams draining impermeable soils are of more uniform chemistry as surface runoff is mainly supplied from the soil zone. Groundwater ANC varies considerably over space and time. In general, the groundwaters have higher ANCs than the ephemeral streams. This is due to increased chemical weathering from the inorganic materials in the lower soils and groundwater areas and possibly longer residence times. However, during the winter months the groundwater ANCs tend to be at their lowest due to additional event-driven acidic soil water contributions and intermediate groundwater residence times.

The results indicate the inappropriateness of a blanket approach to classifying stream vulnerability to acidification simply on the basis of soil sensitivity. However, the results may well indicate good news for the environmental management of acidic and acid sensitive systems. For example, they clearly indicate a large potential supply of weathering components within the groundwater zone to reduce or mitigate the acidifying effects of land use change and acidic deposition without the environmental needs for liming. Furthermore, the high variability of ephemeral stream runoff means that certain areas of catchments where there are specific problems associated with acidification can be identified for focused remediation work for the situation where liming is required.

The case for focused field campaigns and caution against over reliance on blanket modelling approaches is suggested. The results negate the conventional generalizations within hydrology of how water moves through catchments to generate streamflow events (from Hortonian overland flow to catchment contributing areas).

Introduction

Major attention has been given in recent years to using chemical techniques for splitting stream hydrograph responses in relation to rainfall, soil water and groundwater contributions. For example, many studies in isotope hydrology have shown that much of the water entering streams during periods of high rainfall has been in soil and shallow groundwater storage since the streamwater has the isotopic signature of previous rainfall events (Sklash and Farvolden, 1979; Rohde, 1981; DeWalle *et al.*, 1988; Bonnell *et al.*, 1990; Neal and Rosier, 1990; Neal *et al.*, 1992a; Durand *et al.*, 1993). One particularly important hydrograph splitting technique has been End-Member Mixing Analysis (EMMA) which uses chemicals to fingerprint the stream water derived from hydrochemically distinct areas of the catchment such as soil and groundwater stores. These chemical components include base cations, conductivity, acid neutralization capacity (ANC) and Gran alkalinity (Christophersen *et al.*, 1990; Hooper *et al.*, 1990; Neal *et al.*, 1990; Robson, 1993; Hill and Neal, 1997).

Hydrograph splitting techniques using ANC in the upper parts of the River Severn in the Plynlimon area have indicated that groundwater provides an important component to stream flow generation even at times of high flows when soil or rain waters might be expected to dominate (Neal *et al.*, 1990; Robson *et al.*, 1990; Robson, 1993). For these early studies, a groundwater component had not been sampled and a groundwater composition was simply inferred from stream baseflow ANC. Recent work has confirmed that such groundwater occurs within the catchment (Neal *et al.*, 1997a,b). These findings are potentially of major importance for understanding water movement and chemical transfers through upland catchments traditionally thought of as having low ANC, insignificant groundwater transit routes and insignificant storage capacity (Neal *et al.*, 1997a,b).

In this paper, the theme of groundwater supplies to surface water runoff is developed further based on new information on groundwater and surface water runoff chemistry. From this, an assessment is made of (a) the complexity of hydrological groundwater–soilwater flows and (b) the importance of groundwater to stream flow generation, within the Plynlimon catchments.

Rationale and Analytical Details of Hydrograph Splitting Using ANC

ACID NEUTRALIZING CAPACITY

For hydrograph splitting, ANC is used here because (a) it is easily measured with high accuracy, (b) it behaves conservatively on groundwater–soilwater mixing and (c) it provides a clear marker between the soil and the groundwater zone (cf Neal *et al.*, 1990; Robson *et al.*, 1990; Robson, 1993).

ANC is defined, according to Reuss *et al.*, 1986, as

$$\mathrm{ANC} = \Sigma \text{ strong base cations} - \Sigma \text{ strong acid anions} \quad (1)$$

For Plynlimon waters, ANC is approximately given by the equation

$$\mathrm{ANC} \approx [\mathrm{NaH^+}] + [\mathrm{K^+}] + 2[\mathrm{Ca^{2+}}] + 2[\mathrm{Mg^{2+}}] + [\mathrm{NH_4^+}] - [\mathrm{Cl^-}] - [\mathrm{NO_3^-}] - 2[\mathrm{SO_4^{2-}}] - [\mathrm{F^-}] \quad (2)$$

and, using the charge balance constraint,

$$\mathrm{ANC} = \Sigma \text{ weak acid anions} - \Sigma \text{ weak base cations} \quad (3)$$

which is approximated by

$$\mathrm{ANC} \oplus [\mathrm{HCO_3^-}] + \Sigma[\mathrm{Org}_{\text{Anionic charge}}] - \Sigma[\mathrm{Org}_{\text{Cationic charge}}] - \Sigma[\mathrm{Al}_{\text{Cationic charge}}] + \Sigma[\mathrm{Al}_{\text{Anionic charge}}] - [\mathrm{H^+}] \quad (4)$$

For measurement purposes, ANC is determined by the equation

$$\mathrm{ANC} \oplus \mathrm{Alk_{Gran}} - 3{*}\mathrm{Al} + \Delta\mathrm{Org} \quad (5)$$

where $\mathrm{Alk_{Gran}}$, the Gran alkalinity (in μEq l^{-1} units), is a measure of the bicarbonate and, in part, the organic acid buffering less the amount of acidity ($[\mathrm{H^+}]$) in natural waters: Al is the total aluminium concentration (μM) and ΔOrg (μEq l^{-1}) represents the component of organic acid charge not neutralized during the Gran alkalinity titration (Robson, 1993).

$\mathrm{Alk_{Gran}}$ was determined electrometrically for the present study by acidimetric titration in a pH range of 4.0 to 3.0 using a Metrohm autotitrator. In this pH range, $\Delta\mathrm{Org} \oplus 0$. Aluminium concentrations were determined using inductively coupled plasma emission spectroscopy. The analytical protocols and methodology are provided by Neal *et al.* (1988) and Robson (1993) although for these earlier studies the Gran alkalinity was determined in the pH range 4.5 to 4.0. For this higher pH range, ΔOrg can sometimes be more significant. However, initial examination of the results show an insignificant difference between the two methods and there is no problem of incomparability of data. For the present study only data for the acidimetric titration in a pH range of 4.0 to 3.0 is presented.

HYDROGRAPH SPLITTING USING ANC

For the Plynlimon streams, ANC decreases with increasing flow (Figure 1). Under baseflow conditions, stream waters are bicarbonate bearing, of low acidity and contain base cations mainly derived from weathering reactions involving aluminosilicate and carbonate minerals within the bedrock. Under stormflow conditions, a much higher proportion of stream water comes from the soil zone where acidic aluminium bearing conditions apply and where base cation concentrations are low due to (a) the lack of weatherable bedrock components or (b) an insufficiently long residence time or (c) a combination of both (Neal *et al.*, 1990; Robson *et al.*, 1990). Given a knowledge of the groundwater and soilwater 'endmember' ANC concentrations within a catchment, the percentage groundwater within surface runoff can be determined by a two component mixing analysis based

$$\%\text{ groundwater} = 100 * (\mathrm{Anc_{streamwater}} - \mathrm{ANC_{soilwater}}) / (\mathrm{ANC_{groundwater}} - \mathrm{ANC_{soilwater}}) \quad (6)$$

Study Area and Sampling Strategies

The Plynlimon catchments of the upper River Severn and Wye have been the subject of intensive hydrological study since the late 1960s and detailed hydrochemical investigation since the late 1970s (Hornung *et al.*, 1986; Kirby *et al.*, 1991; Reynolds *et al.*, 1984, 1986, 1988, 1989, 1992; Neal *et al.*, 1990a,b, 1992b, 1997a–d; Robson, 1993).

In the present study, the upper parts of the River Severn are examined. Details of the study area are provided by Kirby *et al.* (1991) and Hill and Neal (1997), but as background information for the reader, the following provides details of the basic catchment characteristics. The upper Severn area comprises three major tributaries, the Afon Hafren, the Afon Hore and the Nant Tanllwyth with respective catchment areas of 3.67, 3.08 and 0.89 $\mathrm{Km^2}$ (Figure 2). The upper reaches of the Afon Hafren and Afon Hore, which originate on an extensive plateau of acidic moorland and peat soils, have an altitude range of about 320–740 m.a.s.l. For the lower half of the Afon

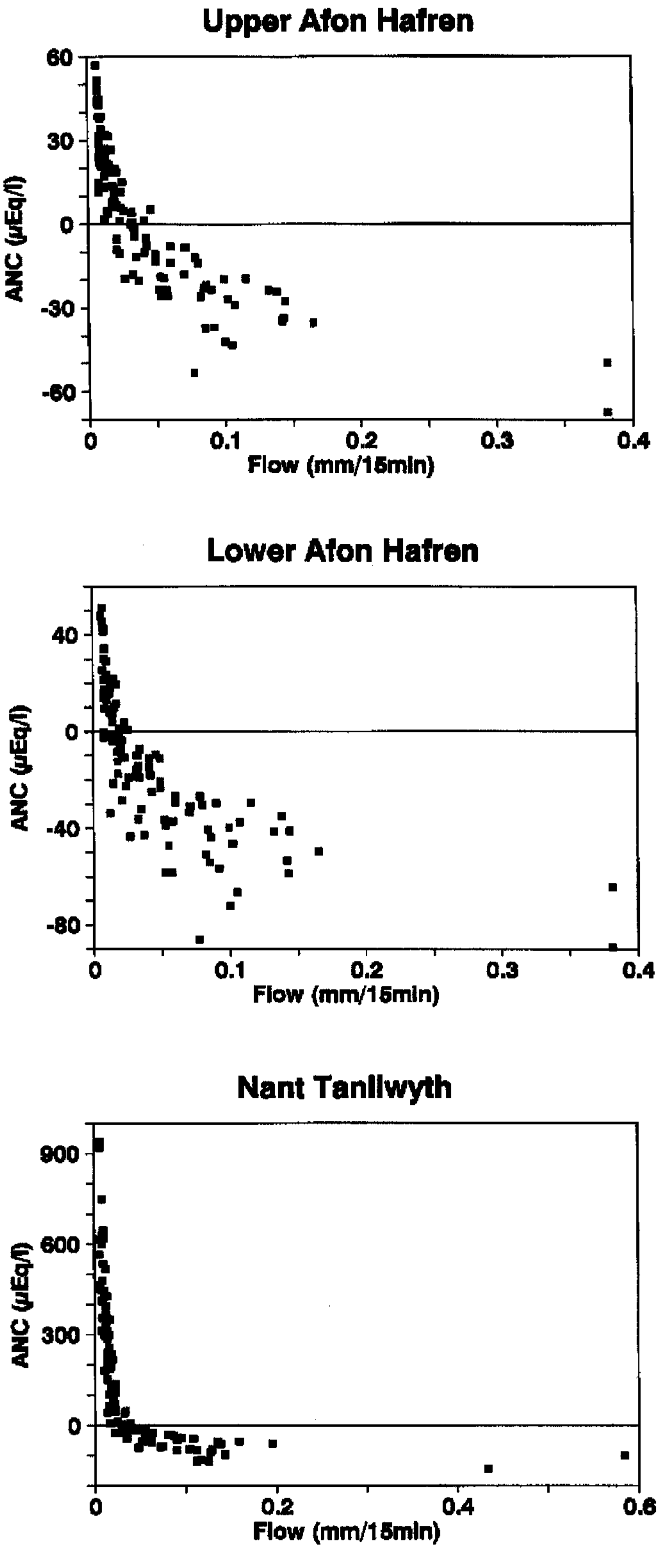

Fig. 1. *Plots of ANC vs stream flow for the upper and lower Hafren and the Nant Tanllwyth. Note in the case of the Tanllwyth, baseflow ANC is particularly high due to the influence of a borehole near to the stream which during development opened up fractures in the rock and increased groundwater supplies: upstream of the borehole, baseflow ANC is about 59 µEq l^{-1} and this compares with a value of about 800 at the downstream point.*

Hafren and Afon Hore, the catchments are associated with plantation spruce forest introduced onto the acid moorland in various phases since the late 1930s. The Tanllwyth catchment is in the lower part of the upper Severn catchment area and is completely forest covered. The underlying geology is comprised of Ordovician and lower Silurian grits and shales, while the overlying soils range from peats, podzols, stagnopodzols to gleys. Apart from minor thinning, tree harvesting has been confined to the lower Afon Hore, where clearfelling occurred between 1985 and 1989. Average rainfall is approximately 2518 mm/yr with evaporation and transpiration losses of 500 to 700 mm/yr and average temperature is 7.3°C. Streamflow response to rainfall is 'flashy' with flow varying by over two orders of magnitude (from less than 0.01 to about 4.5 cumecs for the Afon Hafren and Afon Hore).

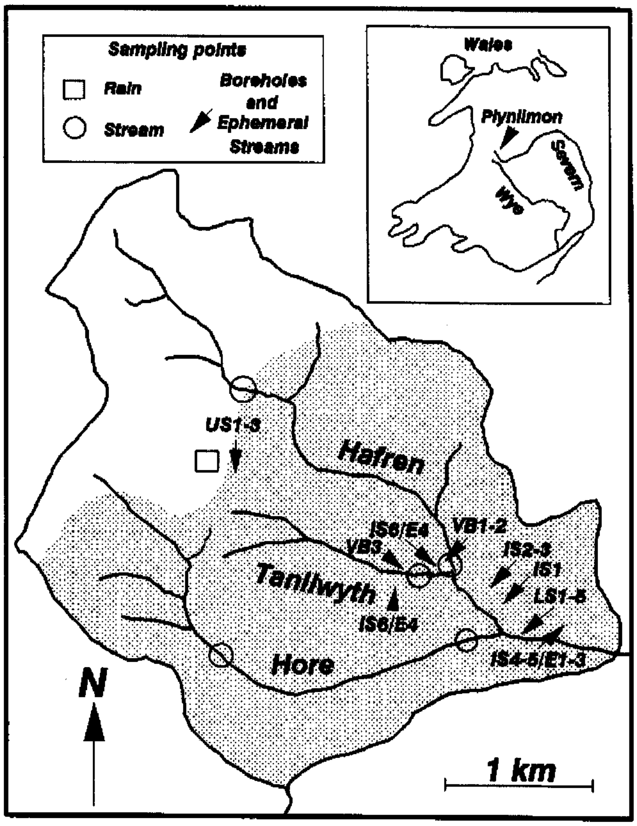

Fig. 2. *The study area.*

The relationship between soilwater and groundwater inputs to stream flow generation is assessed for the present study using information collected on drainage from small ephemeral streams and from shallow boreholes (Figure 2). These data are used to characterise the soilwater and groundwater endmembers, respectively. As information on these compositions is only available for the Hafren and Tanllwyth catchments, only these systems are dealt with here. Also, while the stream waters have been monitored

Table 1. Data monitoring periods for the Hafren catchment: str base and str storm = stream water at baseflow and storm water respectively; bore = borehole; eph str = ephemeral stream.

	Type	Start date	End date
U Hafren	str base	1/1/94	1/1/97
L Hafren	str base	1/1/94	1/1/97
US1	bore	24/4/94	12/7/95
US2	bore	24/4/94	12/7/95
US3	bore	24/4/94	12/7/95
IS1	bore	24/4/94	12/7/95
IS2	bore	24/4/94	12/7/95
IS3	bore	10/5/94	29/10/96
IS4	bore	19/9/44	29/10/96
IS5	bore	10/5/94	29/10/96
LS1	bore	24/4/94	12/7/95
LS2	bore	17/5/94	12/7/95
LS3	bore	24/4/94	12/7/95
LS4	bore	24/4/94	29/10/96
U Hafren	str storm	1/1/94	1/1/97
L Hafren	str storm	1/1/94	1/1/97
E1	eph str	28/4/94	29/10/96
E2	eph str	28/4/94	11/1/95
E3	eph str	11/10/94	15/10/96

for over 10 years, the groundwaters and ephemeral stream waters have only been monitored since 1993 and, consequently, the analysis is confined to data for these later years: sampling periods are given in Tables 1 and 2.

Table 2. Data monitoring periods for the Tanllwyth catchment: Tan-up and Tan-down refer to sampling points upstream and downstream of borehole that affected the downstream chemistry: base and storm = stream water at baseflow and storm water respectively; bore = borehole; eph str = ephemeral stream.

	Type	Start date	End date
Tan up-stream	base	1/8/94	1/1/97
Tan down-stream	base	1/1/94	1/1/97
IS6	bore	5/7/94	29/10/96
IS7	bore	9/8/94	29/10/96
VB1	bore	24/4/94	12/7/95
Tan up-stream	storm	1/1/94	1/1/97
Tan down-stream	storm	1/1/94	1/1/97
E4	eph str	28/4/94	29/10/96
E5	eph str	28/4/94	29/10/96

HAFREN AND TANLLWYTH STREAM SAMPLING SITES

Three upper River Severn sites were studied. These sites are—

(1) **the upper Hafren**: this site provides an integration of drainage for the upper portion of the Afon Hafren. It comprises an area of acid grassland and peat and covers about 41% of the total Hafren catchment area (Roberts *et al.*, 1994);
(2) **the lower Hafren**: this site provides integrated drainage for the main length of the Afon Hafren. It covers a catchment of approximately equal proportion of spruce plantation forest, on predominantly podzolic and stagnopozolic soils, and acid grassland and peat;
(3) **the Nant Tanllwyth**: this is a tributary runoff site downstream of the lower Hafren. The Tanllwyth drains an area completely conifer afforested onto gley and stagnogley soils.

For the lower Hafren and the Tanllwyth sites, samples were taken close to two of the main Institute of Hydrology flumes to provide an accurate measurement of flow: for the upper Hafren, the relative distribution of flows was estimated using data from the lower Hafren site.

During the sampling period, a 45m borehole was introduced near to the Tanllwyth flume to assess deep groundwater circulation patterns near to the stream. As a consequence of this, the Tanllwyth water chemistry changed due to the drilling increasing supplies of alkaline groundwater to the stream 10 or 20 metres upstream of the Tanllwyth sampling point (Neal *et al.*, 1997a,b). For this reason, an additional site was sampled some 20 or more metres above the induced groundwater input.

In all cases, samples were collected from the streams on a weekly basis and stage readings at the flumes were taken within a few minutes of this sampling. The stage readings were then used to calculate the instantaneous flows based on flume calibration information.

SOIL WATER CHEMISTRY

Soil water chemistry varies considerably even over short distances of a few metres (Taugbol and Neal, 1994; Neal and Robson, 1997). Sampling of soil waters directly is labour intensive and there are major question marks over what soil samplers actually measure (Taugbol and Neal, 1994). In the present study, drainage waters from the small first order ephemeral streams have been used to describe the soil drainage component. This approach has been taken as the soil drainage component provides an integrated measure of water actually flowing through the soils and is directly equatable with a scale used within modelling studies (e.g. Christophersen *et al.*, 1982, 1990, Christophersen and Neal, 1990, Neal *et al.*, 1992a).

As there are both relatively free draining (podzolic and stagnopodzolic) and low permeability (gley and stagnogley) soils in the area, ephemeral streams for each soil type were sampled. For each soil type, two first order ephemeral streams were studied in detail as each was to be subsequently used as control and manipulation sites for forest harvesting studies: sites E1 and E3 for free draining soils in the Hafren and E4 and E5 for impermeable soils in the Tanllwyth. However, during the study, one additional site (E2) was monitored on the more free draining soils for part of the time but was then discounted owing to felling commencing earlier than expected. The gley sites are located within the Tanllwyth catchment while the podzol sites are located within the lower portions of the lower Hafren (Figure 2). The sites were sampled fortnightly for water quality.

GROUNDWATER CHEMISTRY

Several sets of shallow boreholes (<15m depth) have been introduced across the Hafren catchment in recent years. The first set comprise a network of eleven exploratory borehole sites across the Hafren catchment covering the upper plateau edge slopes (US1, US2, US3), intermediate slopes (IS1, IS2), lower slopes (LS1, LS2, LS3, LS4, LS5) and valley bottom (VB1) areas (Figure 2). These sites were sampled monthly. To augment this, four additional boreholes were introduced near to the ephemeral stream sites E1, E2, E4 and E5 (IS4, IS5, IS6, IS7): one of the exploratory boreholes (LS4) was used to monitor groundwater near to the ephemeral stream E3 and an additional borehole site, IS5, was also introduced within the Hafren catchment as an additional ephemeral stream monitoring site was originally planned to examine the effects of whole-tree rather than conventional harvesting. These sites were monitored on a fortnightly basis. In addition, three deep boreholes have been introduced near to the Afon Hafren and the Nant Tanllwyth streams (VB2, VB3, LS6) and these were sampled on an irregular basis. The methodologies used for sampling and the sampling depths are described in Neal *et al.*, 1997a,b.

Results

For chemical hydrograph splitting using ANC to be of value for the Hafren and Tanllwyth streams, using the equations given above, soil and groundwater endmember compositions need to remain relatively constant over time and space. Hence, any analysis of the data must begin with an examination of the degree of variability in ANC for the ephemeral stream and groundwater data. Tables 3 and 4 provide summary information for each site to indicate the degree of the variability in the field. These tables indicate that the groundwater is broadly of higher ANC than the ephemeral streams and that the ranges in ANC span the

Table 3. ANC summary data (averages, minimum and maximum values, standard deviations and number of samples) for the upper and lower Afon Hafren (μEq l^{-1} units). Within the table, stream baseflow data is presented next to information on the boreholes. Subsequently, stormflow data is presented next to data for the ephemeral streams in the Hafren catchment. str base and str storm = stream water at baseflow and storm water respectively; bore = borehole; eph str = ephemeral stream.

	Type	Avg	Min	Max	std	N
U Hafren	str base	34.5	11.3	56.8	8.0	16
L Hafren	str base	27.3	–2.4	51.3	16.9	16
US1	bore	3.5	–44.8	81.4	39.1	10
US2	bore	12.2	–1.1	26.9	10.0	9
US3	bore	19.3	–0.1	42.3	11.5	10
IS1	bore	16.2	3.9	35.9	8.6	10
IS2	bore	45.5	6.3	157.7	38.9	10
IS3	bore	440.9	288.4	675.8	81.1	64
IS4	bore	68.7	–0.5	152.1	42.3	37
IS5	bore	104.1	3.6	412.7	99.9	37
LS1	bore	–71.8	–90.7	–57.7	10.3	10
LS2	bore	90.3	16.3	187.4	61.0	10
LS3	bore	11.7	–19.7	89.4	27.2	10
LS4	bore	31.3	–24.8	335.0	71.0	74
U Hafren	str storm	–33.6	–67.3	–19.4	12.1	16
L Hafren	str storm	–50.6	–89.1	–29.3	16.0	12
E1	eph str	41.3	–40.1	95.0	26.4	65
E2	eph str	–31.8	–68.1	9.7	21.0	17
E3	eph str	28.8	–26.6	91.2	20.1	59

Table 4. ANC summary data (averages, minimum and maximum values, standard deviations and number of samples) for the Nant Tanllwyth upstream and downstream of the point where borehole introduction changed stream water chemistry (μEq l^{-1} units). Within the table, stream baseflow data is presented next to information on the boreholes. Subsequently, Nant Tanllwyth data is presented next to data for the ephemeral streams in the Tanllwyth catchment. base and storm = stream water at baseflow and storm water respectively; bore = borehole; eph str = ephemeral stream.

	Type	Avg	Min	Max	std	N
Tan up-stream	base	59.5	31.6	93.4	19.1	10
Tan down-stream	base	579.5	312.2	939.9	183.3	13
IS5	bore	855.0	–233.8	2319.4	714.7	64
IS6	bore	–5.4	–134.3	36.6	27.6	64
VB1	bore	332.0	0.0	3966.2	820.0	10
Tan up-stream	storm	–114.5	–160.1	–88.3	23.6	10
Tan down-stream	storm	–88.7	–144.5	–44.7	27.3	15
E4	eph str	–177.8	–271.4	–46.4	45.7	42
E5	eph str	–156.7	–229.3	–87.4	34.2	34

values encountered within the upper and lower Afon Hafren and the Nant Tanllwyth. However, the table also shows that there is a large range in ANC for each site over time indicating variations in water sources and weathering rates.

There is a marked contrast in ANC for the ephemeral streams supplied by water from the more free draining soils and the impermeable soils. The ephemeral streams draining more permeable soils have compositions which vary over time and from site to site. Two of these ephemeral streams, E1 and E3, have an average ANC which is positive while E2 has an average ANC which is negative. All three ephemeral streams show a variability in ANC from negative to positive values with highest values occurring during dry summer conditions when water residence times are at their greatest and groundwater recharge is low. The ANC values show an approximately normal distribution (Figure 3). The average ephemeral stream water ANC values (about 25 μEq l^{-1}) contrast with podzol soil water charge balance ANCs (estimated using equations 1 and 2) measured elsewhere in Hafren forest (Reynolds *et al.*, 1988). In the soil waters, average charge balance ANC varied between –98 μEq l^{-1} in the surface, organic rich-horizon and –143 μEq l^{-1} in the subsoil B horizon at a depth of between 30–50 cm (Table 5). Ephemeral stream and surface horizon soil water ANCs vary over time according to hydrological conditions within the catchments. The ephemeral streams have their most negative ANC values (–30 to –60 μEq l^{-1}) when the catchments are at their wettest. In the surface soil horizon, soil water ANCs are also at their most negative (–225 to –275 μEq l^{-1}) under wet conditions, although low values have also been observed during re-wetting following short spells of dry weather. Such variations are damped at depth in the soil where there is little clear pattern of temporal variation as the influence of inorganic soil components begins to dominate.

For ephemeral streams associated with free draining soils, the flows cease for only a few weeks in the year, which is indicative of soil/groundwater storage. Given both the unexpectedly high ANC (relative to the soil waters) and the extent of dry weather flow, it must be concluded that a major component of flow throughout the year comes from shallow groundwater sources.

Due to all these observations and companion studies (Hill and Neal, 1997), it seems that the ephemeral streams associated with free draining soils represent at least one soil and one groundwater endmember: both undefined either in terms of fixed or variable chemistry.

The ephemeral streams draining the impermeable soils, E4 and E5, are of much lower average ANC (–178 & –157 μEq l^{-1}) compared to those from the free draining soils (cf. Hill and Neal, 1997). These ephemeral stream waters have ANC values which lie midway between average values observed in soil waters within the upper and lower zones in peaty gley in the Hafren forest; the average charge balance ANC of surface soil waters is –96 μEq l^{-1} compared to –260 μEq l^{-1} in the subsoil (Table 5: data from Reynolds *et al.*, 1992). Charge balance ANC in the surface horizon of the gleys varies in response to soil wetness, but variation is damped at depth. The range of ANC values observed in each soil horizon, whilst comparable between soil types, is much larger than the range of values seen in the ephemeral streams. However, the ANC values are similar for ephemeral streams E4 and E5 and show an approximately normal frequency distribution (Figure 3). As the ephemeral streams dry up during extended dry weather periods, it seems that the main water flow comes from the soil.

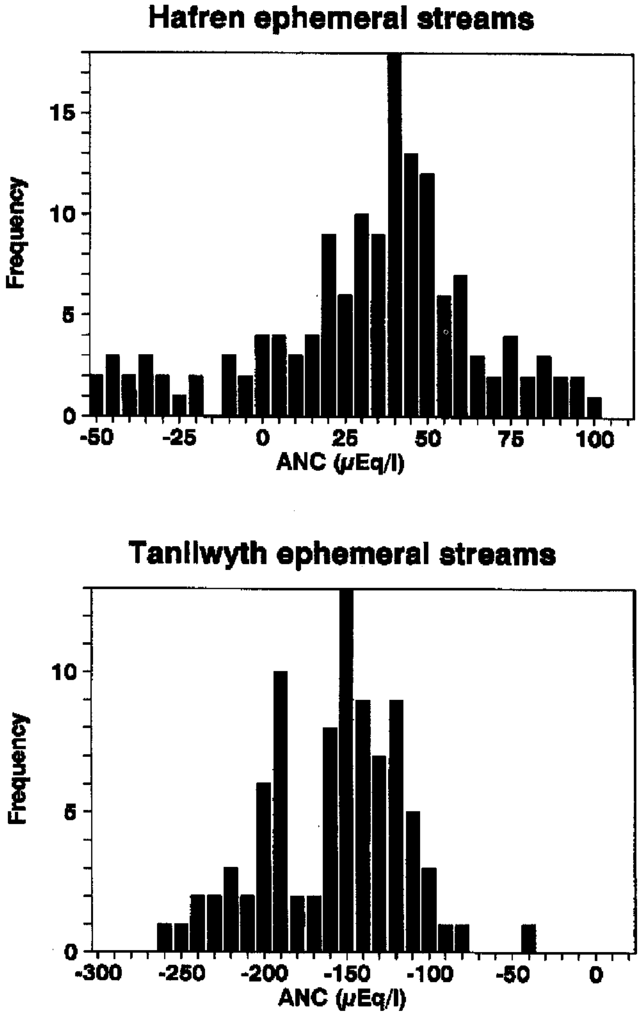

Fig. 3. *The frequency distribution of ANC values for the ephemeral streams in the Hafren and Tanllwyth catchments.*

The use of the ephemeral streams for defining the soil-water endmember composition for the impermeable soils may well be much more appropriate than for the free draining soils case given the reduced variability in ANC.

For the boreholes, there is an extremely large range in ANC. For example, average ANC values between boreholes show ranges of –71 to 104 μEq l^{-1} for the Hafren and –5 to 854 μEq l^{-1} for the Tanllwyth. Furthermore, the range of ANC values for individual boreholes can be very high indeed: typically about –10 to 200 μEq l^{-1}, the extreme example being –233 to 2319 μEq l^{-1} (borehole IS6) in the Tanllwyth catchment and 0 to 3966 μEq l^{-1} (borehole VB1) in alluvial gravels near the juncture of the lower Afon Hafren and the Nant Tanllwyth. For the borehole with the lowest average ANC (LS1), water levels are close to the surface and the main water supplies are probably derived from the soil zone. The boreholes generally show the lowest ANC values during the winter months when on average groundwater levels are at their highest and water supplies clearly must have a component of recently flushed acidic water from the soil zone. However, there is no clear or uniform link between ANC and borehole water level. In the case of the Hafren boreholes, the ANC shows a bimodal distribution (two normal distributions) with peaks at about 10 and 400 μEq l^{-1}. In contrast, the Tanllwyth shows a strongly skewed distribution with a main peak at about 0 μEq l^{-1} and a long tail to very high ANC values of over 2000 μEq l^{-1} (Fig. 4).

Table 5. Summary (averages, minimum and maximum values, standard deviations and number of samples) of charge balance ANC values (μEq l^{-1}) for podzol and gley surface organic O horizon and subsoil B horizon soil waters collected in Hafren forest.

Soil horizon	Avg	Min	Max	Std	N
Podzol O	–98	–366	16	72	61
Podzol B	–143	–555	–19	87	81
Gley O	–96	–340	56	86	55
Gley B	–260	–619	–111	77	82

Discussion

For both the surface and groundwater systems in the upper Severn catchment there is clearly a complex mixture of soil and groundwater sources that varies from location to location in a manner that is not distinguishable directly in the field; geomorphological, geological and vegetational differences seem insignificant. The only clear systematic pattern between soil and groundwater sources is that impermeable soils give runoff of chemistry similar to that for the soil waters, while the more permeable soils have a greater groundwater component in the runoff. With regards to the groundwater chemistry, the huge variability in ANC indicates a highly complex flow routing system with considerable differences in residence times and soil water sources. A very limited number of sites have been monitored and the extreme cases have not been sampled in this study as shown in a companion paper (Hill and Neal, 1997): the variability with a far more detailed sampling network would probably be even higher.

Hydrograph splitting using either two component mixing or end-member mixing analysis (Christophersen *et al.*, 1990; Hooper *et al.*, 1990) cannot be undertaken using the data collected here with any conviction owing to the huge variability in soil, ephemeral stream and groundwater chemistries. Further, the endmember composition of both surface and groundwater changes with time as well as from site to site. This makes chemical hydrograph splitting even more difficult as it requires analysis based on both spatial and temporal variations in soil water and groundwater endmember chemistries.

Despite the variability of ephemeral stream and groundwater ANC, the main Hafren and Tanllwyth streams show much greater regularity. In other words, the catchment

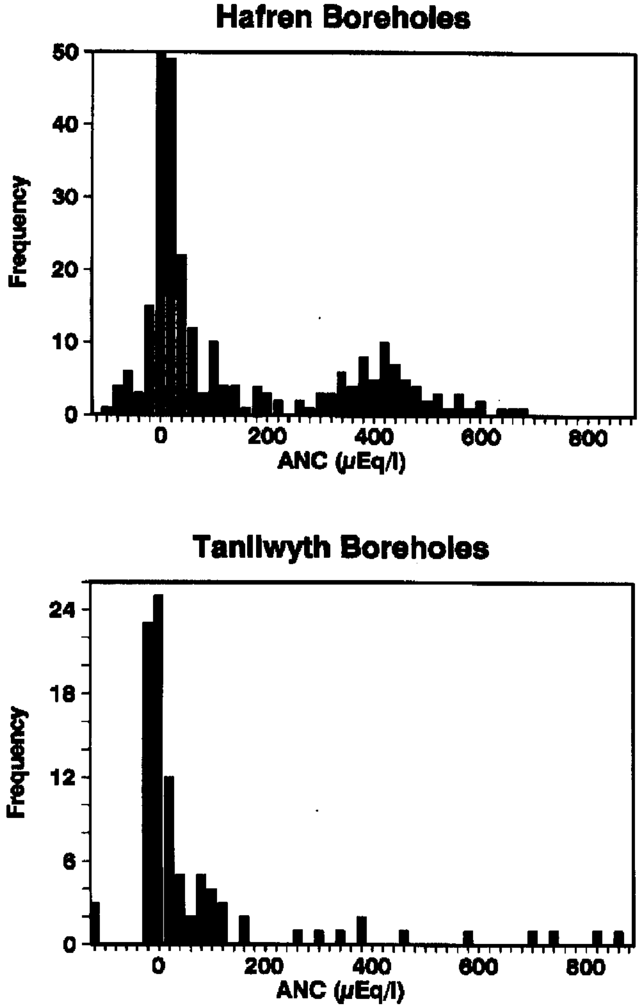

Fig. 4. *The frequency distribution of ANC values for the ephemeral streams in the Hafren and Tanllwyth catchments. Note that in the case of the Tanllwyth, only about 70% of the points are plotted as there is an extensive frequency distribution tail to very high ANC values of over 2000* $\mu Eq\ l^{-1}$.

outlet integrates a complex and highly heterogeneous within-catchment response to produce a simple pattern of behaviour in the main stream channel. On this basis, a pragmatic rule might be to take baseflow as representing solely groundwater inputs from below the soil zone and stormflow chemistry to represent solely soilwater inputs. Indeed, this approach has been used in predicting long term changes in average and extreme stream water quality with changing atmospheric pollution levels (Neal *et al.*, 1992b; Hooper and Christophersen, 1992). Using this approach, eminently sensible results are *apparently* produced for the Plynlimon stream at a *quantitative* level. For example, the volume weighted percentage of groundwater estimated using this approach is respectively about 23, 18, and 10% for the upper Afon Hafren, the lower Afon Hafren and the Nant Tanllwyth: the upper Hafren has a higher proportion of more permeable grits than the lower Hafren (Breward, 1990) whilst the Tanllwyth would be expected to have the lowest groundwater contribution owing to the impermeable nature of the soils. However, the problem with this approach is that it is difficult to explain why the rainfall signal for chemically conservative components is not reflected within the stream during rainfall events: the volumes of water needed to model the soil zone may prove to be greater than the volume of the soil itself (Robson, 1993; Christophersen and Neal, 1990; Christophersen *et al.*, 1993). Thus, the two component endmember approach is not sustained robustly at a quantitative level by observations using other water tracers.

Quantitatively, there are clearly problems with the use of ANC for splitting the hydrograph. However, the qualitative use of ANC as a tracer for soilwater and groundwater supplies is vindicated and multi-element endmember mixing analysis is shown to be a powerful investigative tool for hydrological model testing. Indeed, ANC provides the hydrologist with a means of studying water flow movements through catchments in a way that was not understood properly or utilized even a few years ago. Not only this, but the results negate the conventional generalizations within hydrology of how water moves through catchments to generate streamflow events (from Hortonian overland flow to catchment contributing areas: Neal *et al.*, 1997c).

With regards to modelling acidic environments due to changes in climate, atmospheric deposition of pollutants and land use, the results presented here provide a fundamental challenge both in terms of hydrology and hydrochemistry. This is the case as present techniques lump information together into simple soilwater or soilwater and groundwater units (Christophersen *et al.*, 1982; Cosby *et al.*, 1985a,b; Sverdrup, 1996). From studies of surface water runoff and soil solution chemistries, there are major questions over what the chemical mechanisms involved are within the soils (Neal, 1996) and it is clear that soil chemistry varies spatially with soil type and with depth. This study adds to these concerns by indicating a complex weathering and water transport process within catchments which cannot be predicted quantitatively at the catchment level from laboratory information as some think (e.g. Sverdrup, 1996). The highly heterogeneous nature of catchments are simply not being taken fully into account properly within a modelling framework. For example, kinetic weathering rates for reactive minerals within soil and groundwater areas are strongly linked to water residence times, the volume of the entrained solution and the surface area of water contact with mineral surfaces. However, none of these factors are constant or known with any certainty and they are certainly not measurable at the catchment scale. No matter how much one is swayed by the elegance of existing models, their rapidity of use and their predictions, which seem eminently sensible at the time, there remain many aspects of catchment research that have not been dealt with adequately and field measurement does not reflect model structure. Thus, the need for either (a) more elaborate environmental impact models for describing such a high degree of variability both at the catchment and regional scales or (b) a more critical view of the inherent limitations of current environmental impact models (Hauhs *et al.*, 1996) is overwhelming.

The results presented here may well provide good news to environmental management for acidic and acid sensitive systems. They indicate a large potential supply of weathering components to reduce or mitigate the effects of land use change and acidic deposition without the environmental needs for liming. The key factor in realizing this potential will be (1) our ability to manipulate the hydrological flow pathways in order to supply soil water to the streams via the groundwater zone, and (2) a sufficient degree of weathering to effectively neutralize the increased soil water transfer to the streams via the groundwater zone. The catchments may be manipulated in two ways. Firstly, by changing forest types (e.g. introducing more deeply rooted tree species) and physically breaking through impermeable soil layers to develop and enhance macropore routing through to the groundwater zones. Secondly, by increasing groundwater fracture routes. The first method has not been tried and any manipulative test would require at least two decades of testing in the case of changing tree type (ie to allow tree growth to be established). The second method has, in part, been validated as the ease by which water quality can be improved by groundwater manipulation is evident for the Tanllwyth. At this site, the introduction of a borehole increased high alkalinity groundwater supplies to improve stream water quality dramatically (cf Table 4 and Neal *et al.*, 1997a,b). Not only this, but the large variability in ANC for ephemeral stream runoff means that even if liming techniques are required, certain areas can be identified for focused remediation work (e.g. the highly acidic impermeable soils).

A blanket approach such as critical load mapping to classifying stream and soil vulnerability to acidification simply on the basis of soil sensitivity is not appropriate: the modifying influences of soil texture and the presence of shallow groundwater inputs must be recognised. Shallow groundwater distribution, unlike soil distribution, cannot be readily identified from mapped low intensity survey data (e.g. as on a one to ten or more square kilometre basis). This feature points the way to the requirement for a simple practical approach to determining acid vulnerability which is based on field observation.

The case for continued and focused field campaigns is vindicated and thus the case against over reliance on blanket modelling approaches has become overwhelming.

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