

The application of Strontium isotopes to catchment studies: The Plynlimon upland catchment of Central Wales

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P Shand, D P F Darbyshire and D C Goody



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Geological
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Maclean Building, Crowmarsh Gifford, Wallingford, Oxfordshire OX10 8BB

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Parent Body

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon, Wiltshire SN2 1EU

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1. BACKGROUND

1.1 Introduction

The processes involved in streamflow generation have received considerable attention over the last few decades, primarily in response to concerns about acid deposition and the consequent acidification of streams (Mason, 1990; Likens et al. 1996). The effects of acid deposition on water quality as well as on ecosystem balance depend largely on the ability of catchment materials to neutralise such strong acid inputs, primarily through chemical reaction with soil and bedrock. Much work has also focussed on the transport of agriculturally derived pollutants such as nitrate and pesticides, and on the effects of land-use change (e.g. afforestation, deforestation). Fundamental to modelling the response of catchments to these environmental changes is a knowledge of the water flowpaths and the source and behaviour of solutes in groundwater and through the soil and unsaturated zone. The water flowpaths and sources will vary both seasonally and during storm events making solute-transport modelling difficult.

Water falling on a catchment undergoes significant chemical changes through reaction with biotic and mineral surfaces. The chemical evolution of this water is strongly influenced by the specific pathways and residence time in the catchment. The complexities of the shallow hydrological system such as large variations in soil type, biomass and geology have meant that there has been considerable, and as yet largely unresolved debate concerning flow mechanisms and solute transport even through relatively simple catchments.

Acidic atmospheric deposition (natural and anthropogenic) is neutralised within catchments by a two step process (Johnson et al., 1981): initial uptake of hydrogen ion acidity takes place through exchange with reactive Al in the soil and is followed by exchange of Al and protons by base cations in the soils and due to bedrock weathering. The soil base cation pool is important in buffering acidic inputs to catchments through rapid ion-exchange reactions. In a system at equilibrium, the release of cations through weathering is balanced by acidic inputs. The soil base cation pool is important in the buffering of acidic inputs to catchments primarily through rapid ion-exchange reactions. This pool is, however, limited and excess inputs act to deplete the pool, leading ultimately to serious damage to local ecosystems. Although ion exchange reactions may control short term fluctuations, long term change is controlled by mineral weathering which regulates the primary production and release of base cations to the soil. Therefore, the ability of catchments to buffer acid inputs is fundamentally controlled by the geology and soil type of the catchment. Areas where the bedrock is depleted in base cations or where weathering rates are slow (acid igneous and metamorphic rocks) are most at risk from such pollution. In a study of soils from southern Sweden, Falkengren-Grerup & Tyler (1992) concluded that silicate weathering did not keep pace with biomass uptake and leaching. Weathering rates are, therefore, a fundamental control on the long-term response of catchments to environmental change. In parts of upland Britain, especially where bedrock is depleted in base cations, the soil pool may be strongly influenced by precipitation inputs in addition to weathering (Shand et al., 1997; White et al., 1998).

1.2 Natural tracers

A wide range of tracers, both natural and anthropogenic, have been used to gain a better understanding of the flow mechanisms in catchments. Perhaps the most useful tracers in catchment hydrology are the stable isotopes $\delta^{18}\text{O}$ and $\delta^2\text{H}$ because they are constituents of the water molecule and therefore, tracers of the water itself. In addition, they behave conservatively in low temperature environments in the sense that interactions with catchment materials will have little effect on the isotopic composition of the water. Solute stable isotopes (S, N) have also been extremely useful in indicating the various chemical pathways,

sources and processes that occur in the catchment. More recently, the radiogenic isotopes of Sr and Pb have been used to estimate weathering rates or sources of these elements in stream waters (Graustein & Armstrong, 1983; Åberg et al., 1989). These isotope ratios are extremely useful because they are not fractionated by geochemical reactions (e.g. mineral dissolution and precipitation) or biotic processes, and may be used to investigate mineral weathering reactions. Differences in isotope ratios reflect only mixing, thereby providing valuable information on sources and geochemical processes. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in streams and rivers varies widely, with values as low as 0.7046 in young basaltic terranes (Wadleigh et al., 1985) up to 0.7456 in granitic terranes of Proterozoic age (Åberg & Wickman, 1987; Åberg et al., 1989). The importance of bedrock type and age in controlling the variation in isotope ratios was highlighted by Wadleigh et al. (1985), who found contrasting isotope signatures in a study of 39 major Canadian rivers.

Unlike $\delta^{18}\text{O}$ and $\delta^2\text{H}$, Sr isotopes can change through reaction with minerals and so indicate chemical reactions which have taken place in the catchment. Solute tracers primarily provide information about the solute measured and not necessarily the water itself. Strontium in runoff, soils and biomass will be a function of mixing between atmospheric inputs and mineral weathering. Differences in solute Sr isotope ratios are controlled by variations in initial inputs, differences in mineralogy along flowpaths, mineral dissolution characteristics and residence time. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in waters will therefore be a function of the "weatherable Sr" and the efficiency of exchange (Åberg et al., 1989). These ratios often show relatively little variation in stream waters, and the isotope ratio in runoff reflects a balance between the long term input ratio from atmospheric deposition to that mobilised through weathering (Jacks et al., 1989). One of the main problems is in defining the isotope composition of this weathering-derived Sr. Complete rock or soil dissolution does not give a fair representation of the weathering ratio because of the different weathering rates and stabilities of minerals in the weathering environment. The whole rock isotope ratio is of little relevance in determining weathering rates because the weathering-derived ratio will be dominated by those mineral phases with the highest dissolution kinetics. Therefore, a range of leachate and extraction techniques, usually employing organic acids, have been used to determine the weathering component of Sr in soils (Åberg et al., 1989; Wickman & Jacks, 1992; Miller et al., 1993). The presence of different mineral phases and different water flowpaths necessitate considering isotope data in conjunction with solute chemistry.

Strontium isotopes have also been used to estimate directly weathering rates of Sr, and also as a surrogate for the essential alkali earth element Ca (Jacks & Åberg, 1987), based on the assumption that calcium exhibits the same ratio of deposition to weathering as strontium (Jacks et al., 1989). Although Sr generally behaves similarly to Ca, minerals may have significantly different Sr/Ca ratios and, therefore, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios may not necessarily be a precise indicator of Ca sources (Kendall et al., 1995; Shand et al., 1997). Wickman & Jacks (1992) emphasised that, in order to improve the application of Sr isotopes to weathering studies, a knowledge of Sr isotope signatures is required for different parts of catchment.

1.3 Weathering in catchments

Rates of chemical weathering are generally derived through a catchment mass balance, but the use of isotope ratios may allow the inputs from atmospheric and weathering components to be differentiated. During weathering, the most reactive minerals (e.g. carbonates, mafic minerals and calcic plagioclase) contribute a disproportionate amount of dissolved species to the water. The value of $^{87}\text{Sr}/^{86}\text{Sr}$ in local streamwaters will be strongly influenced by the most easily weathered phase which will generally have a different Sr isotope signature from that of the whole rock. Although it is often assumed that the weathering-derived ratio of $^{87}\text{Sr}/^{86}\text{Sr}$ is constant, this is likely to be the case only in monomineralic terranes. The early stages of weathering in some terranes has been shown to be dominated by dissolution of the most reactive minerals (e.g. biotite, plagioclase) and the contributions of Sr may therefore vary with the age of the soil (Bullen et al, 1995; White & Blum, 1995). In recently glaciated terrains or areas where mechanical weathering is rapid (Stallard & Edmond, 1983), this is likely to be a major factor because soils will be relatively young. The production of base cations in catchments due to chemical weathering is important

because of their role as plant nutrients, in neutralising acidity or generating alkalinity and in the replenishment of the soil ion exchange pool. The geology and mineralogy of catchment rocks, therefore has a large effect on solute concentrations, e.g. the effects of acid deposition are largely controlled by the composition of the underlying bedrock (Box 1).

Knowledge of the sites of weathering on a both a microscopic and macroscopic (e.g. catchment) scale is important for the effective management of water resources and ecosystems. There are usually discrepancies between laboratory and field based methods of estimating weathering rates, with the former often being an order of magnitude higher. A major factor is the differences between the two methods in the exposure of mineral surfaces to water as a result of variable flow paths and inhomogeneities in soils (Velbel, 1993; Berner & Berner, 1996).

Weathering rates may be calculated by determining the output of solutes from a closed system catchment and subtracting inputs. This requires detailed knowledge of all contributing sources and pathways. Some inputs, e.g. dry deposition, are poorly constrained and such inputs are generally calculated by deduction rather than directly. One of the problems in determining mixing/mass balance calculations in such a complex system as a river catchment is the inability to uniquely characterise the various reservoirs in the system. Detailed stable and radiogenic isotope studies may provide valuable information with regard to the source and origin of individual solutes and pathways through the catchment. The use of Sr and other radiogenic isotopes has been limited in most fields of hydrogeochemistry, but recent studies have highlighted the application of Sr isotopes as a tracer and indicator of geochemical processes, particularly when combined with other hydrochemical data. Miller et al. (1993) have also attempted to discriminate weathering rates from exchangeable cation loss based on Sr isotopes. In comparison with many fields of isotope geochemistry, there is a paucity of data and limited understanding of the application of strontium isotopes to natural waters.

1.4 Aims of report

The aim of this study is to assess the use of strontium isotopes in determining flow pathways, weathering rates and the rôle of groundwater in streamflow generation in the upland catchment of Plynlimon in Central Wales. The potential and limitations of the application of radiogenic isotopes in such studies have not yet been fully evaluated. Collaboration between scientists in the fields of radiogenic isotope geochemistry and catchment hydrogeochemistry is at an early stage and the present report will provide introductions to both fields in the hope that its use may be extended to those not familiar with one or the other.

The report documents the following:

- a) the source of strontium and characterisation of Sr reservoirs within catchment
- b) the identification of flowpaths during different flow regimes in the catchment
- b) the mechanisms of streamflow generation
- d) weathering reactions
- e) weathering rates
- g) the role of groundwater in streamflow generation

The important effects of biogeochemical cycling of Sr (Åberg, 1995) have not been included but would form an essential aspect of further work required to understand fully the role of biomass in controlling Sr fluxes. The physical components of flow and catchment processes are briefly described in section 2 and the isotope systematics of two component mixing outlined in section 3. A summary of the Plynlimon site and sampling and analytical techniques are given in section 4 and the results presented in section 5. The application of the data to problems of flow determination and weathering rates are discussed in sections 6 and 7 respectively, and conclusions drawn are presented in section 8.

BOX 1: CHEMICAL WEATHERING

Chemical weathering is the term used to describe the low temperature transformation of minerals formed at particular P – T conditions within the earth into more stable secondary minerals and solute species through interaction with dilute waters close to the earth's surface. In general, there are three products of the weathering process:

- Solute species
- Secondary minerals e.g. clays, oxides
- Residual unweathered materials e.g. quartz

The weathering of a rock can be described simply by a general mass balance:

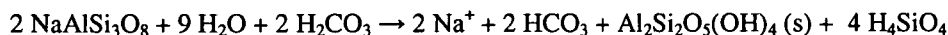


The ability of rainfall to dissolve minerals is largely due to the fact that it is slightly acidic because of the presence of dissolved carbon dioxide (producing carbonic acid) derived from the atmosphere. Soil waters may be more acidic due to increased levels of carbon dioxide from biological activity and the decomposition of organic matter. The presence of strong acid components due to industrial pollution may give rise to "acid rain" which will cause increased weathering rates. The chemical processes which control weathering include hydration, hydrolysis, redox reactions and complex formation, although the exact mechanisms are poorly understood in detail.

The term applied to the process where a mineral dissolves completely is **congruent dissolution** in contrast to **incongruent dissolution** where only part of the mineral dissolves. A typical congruent reaction is typified by the dissolution of calcite:



Silicate minerals generally dissolve incongruently at the pH values typical of natural waters e.g. during the dissolution of feldspars, solute cations and silica are formed along with residual clay minerals such as gibbsite or kaolinite:



The different minerals present in rocks show an extremely wide range of weathering rates covering several orders of magnitude. The relative reactivity of common minerals increases in the order quartz > albite > mafic silicates > anorthite > carbonates. One consequence of this is that weathering is highly selective and the most reactive minerals (e.g. calcite, anorthite) will contribute a disproportionate amount of dissolved species to the water. The presence of calcite, for example, may dominate the chemistry of water even if present as a minor component of the rock.

The production of base cations in catchments due to weathering reactions is important because of their role as plant nutrients, in neutralising acidity or generating alkalinity and in the replenishment of the soil ion exchange pool. The geology and mineralogy of catchment rocks, therefore has a large effect on solute concentrations in water as well as being an important control in buffering chemical changes imposed through environmental change.

from groundwater. Spatial and temporal differences may also exist within some components particularly in the soil waters. The application of stable isotopes to hydrograph techniques has shown that pre-event water may form a major component of discharge even during storm events (Fritz et al., 1976; Sklash & Farvolden, 1979). Such results indicate that displacement of this 'pre-event' water by rainfall is a major process controlling streamflow generation. The importance of groundwater as a major source of water and solutes to lakes and streams is being increasingly recognised (O'Brien, 1980; La Baugh et al., 1995).

2.2 Catchment processes

Many studies have concluded that several potential sources within the catchment contribute to streamflow (Fritz et al., 1976; Kennedy et al., 1986; DeWalle et al., 1987; Christopherson et al., 1990). One of the problems with mixing calculations using chemical parameters is that relatively few solutes are conservative, and it is often difficult to discriminate between reaction and mixing. The importance of rapid ion exchange reactions in the soil zone, for example, makes estimation of the end members difficult. One of the most intriguing observations in catchment studies is that several solute concentrations show a damped response in comparison to the large range in atmospheric inputs and flow conditions: extremely large changes in discharge show little change in solute concentration (Fritz et al., 1984; Neal et al., 1992). This can be explained in a number of ways including buffering through ion-exchange/dissolution reactions or displacement of a hydraulically active, longer residence time groundwater. The relationship between flow and solute concentration is generally complex, and for the same discharge, the solute chemistry can be different between flood and recession periods (Fritz et al., 1984). Sharp declines in pH, Ca, Mg, Na and Si are often observed with increasing flow, whereas Al, Fe, Mn, K and organic C often show the reverse trend. The phenomenon of decreasing concentrations with increased flow is generally attributed to dilution effects, but a recent study (Anderson et al., 1993) has shown that this apparent dilution occurs whether the input is rainwater or artificially applied sprinkler water containing high solute concentrations. In the latter case, this apparent dilution was interpreted as due to rapid exchange reactions in the soils which buffered the concentrations of solutes. However, the conclusions from stable isotope studies indicate that the discharge to rivers is mainly by displacement of stored water and the problem of reaction versus displacement of older water remains unresolved. It is likely that both mechanisms are important depending on the antecedent conditions and amount of precipitation. The role of discharge is important in controlling the total outputs or flux of elements, and at higher flows there is generally an increase in flux despite inverse correlations between concentration and flow (Edwards et al., 1984).

Biomass may have a significant effect on some elements, particularly in forested regions where uptake and storage by trees may account for up to 50 % of weathering derived elements (Likens et al., 1977). The catchment budget of solutes is greatly affected by the uptake, storage and release of nutrient elements in biomass. Since the uptake of cations by trees is greater than anions there is a net release of hydrogen ions to sustain charge neutrality. Soil acidity is also produced through the activity of soil micro-organisms, and combined with root exudation, is the dominant contributor to hydrolysis and exchange reactions in soils. It has often been assumed in catchment studies that the forest is in steady state growth. Although this is often an invalid assumption (Taylor & Velbel, 1991), it is a simplification that allows solute losses to be equivalent to release by chemical weathering. Following felling, branches and twigs are generally left in the catchment, but the removal of stemwood and bark represents a permanent loss (Åberg et al., 1990).

Solute mass balances have been extensively used (Paces, 1983; Velbel, 1985) to provide data for the weathering and mobility of solutes in catchments and are based on chemical flux (Q) measurements:

$$Q_i = C_i \frac{V}{A.t}$$

where C_i is the chemical concentration, V is the fluid mass, A is the area of the catchment and t is time. The chemical mass balance is then calculated by the relationship:

$$Q_w = Q_{dis} - Q_{precip} - Q_{dry} \pm Q_{bio} \pm Q_{exch} \pm Q_{gw}$$

where

- Q_w = net solute flux from sources within the catchment (weathering)
- Q_{dis} = output flux in stream discharge
- Q_{precip} = input flux from wet deposition: collected rainfall
- Q_{dry} = input flux from dry deposition
- Q_{bio} = input or output flux based on biomass release or uptake
- Q_{exch} = input or output flux based on change in ion exchange pool
- Q_{gw} = input or output flux based on change in groundwater storage

Stream discharge and wet deposition are relatively straightforward to measure but dry deposition is technically much more difficult and calculation is often based simply on a conservative element (generally chloride) mass balance, using rainfall and stream output fluxes. Biomass uptake or release will occur where aggrading or degrading forests are present, and although steady state is often assumed, the actual corrections may be significant (Taylor & Velbel, 1981). Similarly, changes in exchangeable ions may be influenced by biomass and therefore long term fluxes are used which assume steady state over long time periods. However, decreases in the store of exchangeable cations have been noted in some Swedish soils, with the reduction being related to acid deposition (Falkengren-Grerup & Tyler, 1992). Most small catchment studies have been in hard rock areas which are considered to be essentially impermeable, so it is assumed that the basin studied is a closed system and the term Q_w has been generally ignored. Long term flux measurements ensure that errors due to changes in groundwater storage (Q_{gw}) are minimal.

The benefits of applying strontium isotope ratios to problems in catchment hydrology and weathering lie in the fact that they are not fractionated during chemical reactions or mixing at low temperature. Provided there is significant variation in isotope signature between potential end members, the contribution of individual sources can be modelled. If Sr in water of a particular source is found along a flow path then it must be hydraulically possible for that source to have contributed to this flowpath. However, a particular isotope composition may result from the mixing of more than two components and the solution may not be unique. Strontium isotope studies can provide valuable information on weathering in small catchments because Sr is ultimately derived from only two sources: atmospheric inputs and weathering inputs. Providing that the isotope composition of these sources is relatively homogeneous, a reasonable estimate of atmospheric and weathering proportions can easily be calculated.

3. STRONTIUM ISOTOPE SYSTEMATICS AND MIXING

The alkaline earth element Sr has four natural isotopes: ^{84}Sr , ^{86}Sr , ^{87}Sr and ^{88}Sr , all of which are stable. However, the isotopic abundances are variable because of the formation of radiogenic ^{87}Sr by the beta decay of naturally occurring ^{87}Rb which has a half-life of 4.88×10^{10} years (Faure, 1977). Geological processes such as partial melting, fractional crystallisation, metamorphism and low and high temperature alteration allow bulk fractionation of Rb from Sr, leading to different Rb/Sr reservoirs. The individual minerals, which constitute a rock, will generally have widely different Rb/Sr ratios as a consequence of the preferential partitioning of Rb and Sr into different mineral phases. In systems where minerals have formed with identical $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, ^{87}Rb decay will lead, with time, to minerals with different $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Rb-rich minerals will develop higher $^{87}\text{Sr}/^{86}\text{Sr}$ in proportion to the value of the Rb/Sr ratio than those which are Rb-poor. Biotite has a very high partition coefficient for Rb in fluids and magmatic systems, but a low coefficient for Sr (giving it a high Rb/Sr ratio) which leads in time to high $^{87}\text{Sr}/^{86}\text{Sr}$, whereas plagioclase strongly partitions Sr but not Rb and typically has a low $^{87}\text{Sr}/^{86}\text{Sr}$. In general, older rocks with high Rb/Sr ratios will develop mineral phases with the highest ratios. A comprehensive discussion on the dating of minerals and rocks by the Rb-Sr technique is given by Dickin (1995).

Strontium is present in seawater with a concentration of about 8 mg kg^{-1} . The marine isotope composition is determined by mixing of unradiogenic Sr from the erosion of young volcanic rocks and submarine hydrothermal exchange with basaltic crust, radiogenic Sr from old continental crust and Sr of intermediate composition from carbonates. The residence time of Sr in the oceans is much higher (4×10^6 years; Stumm & Morgan, 1996) than the ocean mixing time (ca. 10^3 years) resulting in an isotope ratio that is essentially constant at any given time. Recent advances in mass spectrometry have allowed the construction of a high precision seawater Sr isotope evolution curve which shows that the ratio has decreased during the Palaeozoic, reaching a minimum during the Mesozoic before rising to the present day value of 0.7091 (see Dickin, 1995 and references therein). These changes reflect the complex interaction of the competing fluxes.

In freshwater systems, the residence times of waters are sufficiently low (days to 10^{2-3} years) compared to the half life of ^{87}Rb (10^{10} years), that radiogenic decay of ^{87}Rb can be ignored. Sr isotopes are particularly useful natural tracers due to the lack of fractionation by biological or chemical processes and mixing is simply a function of mixing between different reservoirs. One of the main problems of mixing calculations which require solute 'concentrations' to estimate end-member compositions, is the assumption that chemical processes operating along flowpaths between the source and catchment outlet are insignificant (Chapman et al., 1993). However, isotope ratios are source dependant and therefore provide information on the geochemical processes which occur along the flowpath.

Mixing processes are the dominant means of producing variations in radiogenic isotopes in most natural systems. The chemical and isotope systematics of mixtures can be treated mathematically (Faure, 1986), but application of these models is valid only where the resultant compositions are not changed by subsequent processes. In two component mixtures, the concentration of an element X in the mixture of two end members A and B, is given by:

$$X_M = X_A f + X_B (1 - f)$$

where the mixing parameter f is defined as:

$$f = \frac{A}{A + B}$$

Several authors (e.g. Graustein, 1989) have used the relation $^{87}\text{Sr}/(^{87}\text{Sr} + ^{86}\text{Sr})$ because this ratio has the property that:

$$\frac{^{87}\text{Sr}}{(^{87}\text{Sr} + ^{86}\text{Sr})_A} f + \frac{^{87}\text{Sr}}{(^{87}\text{Sr} + ^{86}\text{Sr})_B} (1-f) = \frac{^{87}\text{Sr}}{(^{87}\text{Sr} + ^{86}\text{Sr})_M}$$

Solving the equation for f , the fraction of Sr in the mixture gives:

$$f = \frac{\frac{^{87}\text{Sr}}{(^{87}\text{Sr} + ^{86}\text{Sr})_M} - \frac{^{87}\text{Sr}}{(^{87}\text{Sr} + ^{86}\text{Sr})_B}}{\frac{^{87}\text{Sr}}{(^{87}\text{Sr} + ^{86}\text{Sr})_A} - \frac{^{87}\text{Sr}}{(^{87}\text{Sr} + ^{86}\text{Sr})_B}}$$

The ratio $^{87}\text{Sr}/(^{87}\text{Sr} + ^{86}\text{Sr})$ is related to $^{87}\text{Sr}/^{86}\text{Sr}$ by:

$$\frac{^{87}\text{Sr}}{(^{87}\text{Sr} + ^{86}\text{Sr})} = \frac{\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)}{1 + \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)}$$

In environmental studies, the isotope composition of Sr has been normalised to a reference standard with values reported as Δ or δ values. However, these parameters are sometimes confused. The δ notation is derived by analogy to the method of reporting stable isotope data and is defined as:

$$\delta^{87}\text{Sr} = \left[\left(\frac{\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{sample}}}{\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{standard}}} \right) - 1 \right] \times 10^4$$

where the standard is usually modern seawater.

However, the symbol Δ is often used to indicate that the isotope composition of the samples are expressed relative to an arbitrary local standard so that samples within an ecosystem may be compared. Then:

$$\Delta^{87}\text{Sr} = \left[\frac{^{87}\text{Sr}}{(^{87}\text{Sr} + ^{86}\text{Sr})}_{\text{sample}} - \frac{^{87}\text{Sr}}{(^{87}\text{Sr} + ^{86}\text{Sr})}_{\text{standard}} \right] \times 10^4$$

Graustein & Armstrong (1983) used the value of the rainfall (0.7088) measured in their study as a

normalising standard, whereas Bullen et al. (1996) used the value of the NBS 987 standard reference material. The lack of an agreed normalising value makes comparison between different datasets difficult and confusing, but there is as yet no consensus on an internationally agreed standard. The authors would prefer use of the ratio of average modern seawater: firstly, the isotopic signature of rainfall (the source of surface and groundwater) is typically similar to the marine signature because most rainfall solutes are derived from seawater, and secondly, it provides a basis for comparison to initial inputs and subsequent chemical evolution. The mean value of modern North Atlantic seawater determined during the course of this study was 0.709172 ± 0.000014 ($n = 40$) and would form a good reference. The normalisation to measured values of such a reference material would also reduce analytical errors found between different laboratories.

$\Delta^{87}\text{Sr}$ then has the properties that:

$$\Delta^{87}\text{Sr}_M = f \Delta^{87}\text{Sr}_A + (1-f)\Delta^{87}\text{Sr}_B$$

Weathering rates have been determined by Wickman & Jacks (1992) using the expression:

$$W \% = \frac{\left[\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_R - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_D \right]}{\left[\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_W - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_D \right]} \times 100$$

where R, D and W refer to runoff, deposition and weathering respectively. If it is assumed that Sr and Ca behave similarly, then the rate of Ca weathering can then be calculated from:

$$\text{Weathering rate} = D_{Ca} \times \frac{W \%}{(100 - W \%)}$$

The above equations are valid providing that only two components (A and B) are responsible for the variation in the system of interest. Such mixing equations are used to calculate the proportions of Sr derived from each of the end-members (e.g. weathering-derived and atmosphere-derived) but does not allow calculation of the catchment components (e.g. proportions of rainfall and soil-water or groundwater). Mixing equations for isotope ratios can be combined with Sr concentrations to provide information concerning the quantities of the actual components mixing, and not simply the Sr itself. Again this again requires that the elements behave in a conservative manner during the mixing process and that changes have not occurred after mixing. Therefore, end member concentrations, as well as the isotopic ratios, are necessary.

The equations describing mixing are found in Faure (1986):

$$f = \frac{Sr_B \left[\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_B - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_M \right]}{\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_M (Sr_A - Sr_B) - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_A Sr_A + \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_B Sr_B}$$

The isotope ratio of a mixture is then calculated as:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_M = \frac{Sr_A Sr_B \left[\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_B - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_A \right]}{Sr_M (Sr_A - Sr_B)} + \frac{Sr_A \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_A - Sr_B \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_B}{Sr_A - Sr_B}$$

The above equations are used to estimate the contributions from atmospheric inputs and weathering in the Severn catchment and in the nested catchments of the Hafren, Hore and Tanllwyth.

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The isotope ratio of a mixture is then calculated as:

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The above equations are used to estimate the contributions from atmospheric inputs and weathering in the Severn catchment and in the nested catchments of the Hafren, Hore and Tanllwyth.

4. BACKGROUND, SAMPLING AND ANALYTICAL TECHNIQUES

4.1 The Plynlimon Site

The Plynlimon experimental catchment (Figure 4.1), approximately 16 miles northeast of Aberystwyth, has been a research site since the early 1970's. Detailed information regarding the Plynlimon catchment study has been presented by Kirby et al. (1991). Much of the early hydrochemical work focussed on the effects of land use change on water quality (Neal et al., 1992). The Afon Hafren and Afon Hore catchments form the two main headwater sub-catchments of the river Severn: they are of similar size, about 340 ha, with elevations of 350 - 750 m above sea-level. The catchment is largely forested, mainly with Sitka Spruce but with semi-natural moorland in the upper reaches above the tree line. Mean annual temperature is 7.2 °C and rainfall in the area is around 2500 mm, most (nearly 75 %) of which is derived from synoptic westerly air masses. The area has been strongly influenced by the effects of Quaternary glaciation and periglaciation (Newson, 1976). There is limited development of valley flat areas with alluvial reaches (Kirby et al., 1991).

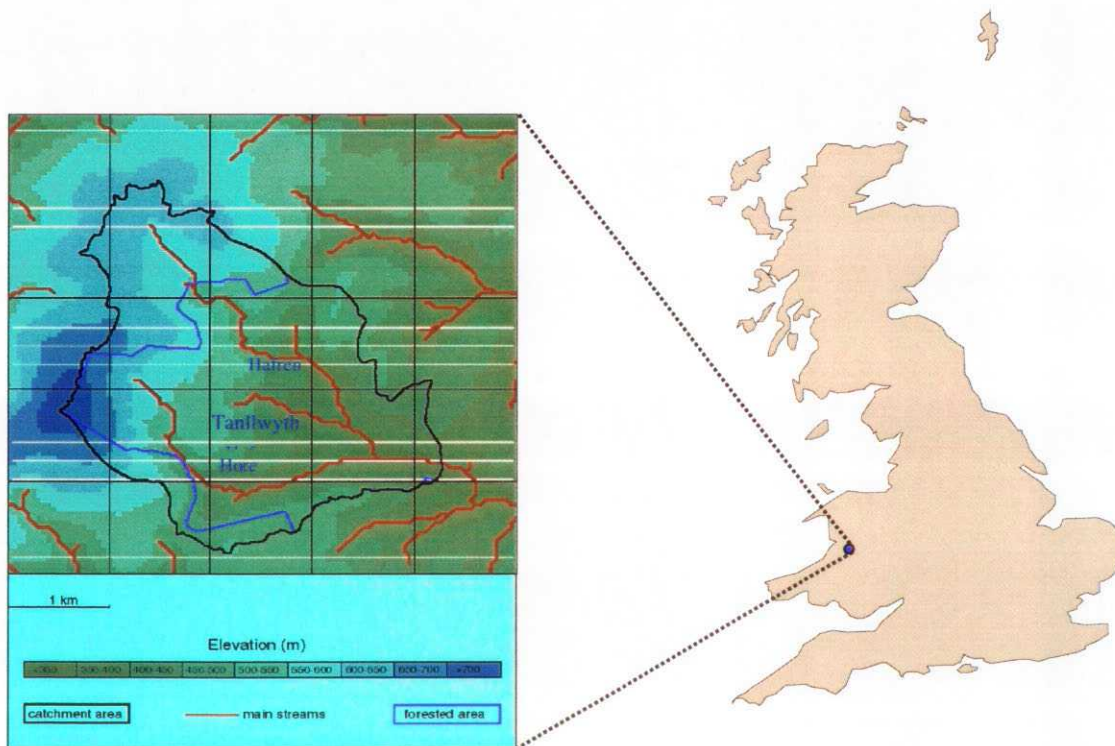


Figure 4.1 Map showing location of study area and headwater streams of the River Severn.

Lower Palaeozoic mudstones dominate the bedrock geology with sandstones and grits present in the upper part of the catchment. The mineralogy of the mudstones comprises an iron magnesium chlorite, a dioctahedral mica and quartz, with lesser amounts of feldspar and iron oxides (Hornung et al., 1986). The catchment is covered with thin (0.5 - 1.0 m) acidic soils, mainly podzol in the free draining areas and peat on the flat upper parts of the catchment and wider interfluves (Figure 4.1). The valley bottoms where drainage has been impeded contain a complex of peat and gleyed mineral soils (Kirby et al., 1991). Soil mineralogy is closely related to the bedrock but with alteration of the chlorite and transformation of illite to vermiculite. Chlorite is relatively rare in the upper soils but increases with depth, in contrast to vermiculite, which is high in the upper parts of the soils.

Catchments on metamorphic or igneous rock types have generally been assumed to be impermeable, with physical and chemical variations being interpreted in terms of the shallow hydrological system (soils) above the bedrock. This has also been the case with the Plynlimon catchments. The role of groundwater in such studies has largely been ignored and assumed to play an insignificant role in controlling streamflow generation and hydrochemistry.

4.2 Previous geochemical studies

The objectives of geochemical research in the Plynlimon catchments were to identify hydrological pathways, chemical changes during deforestation and to categorise the major hydrochemical processes (Kirby et al., 1991; Neal et al., 1992). This was done mainly by monitoring selected sites where flumes had been installed for hydrological investigations. The Plynlimon streams show a very flashy response to rainfall events and significant changes in streamwater chemistry with stream flow. A large number of geochemical studies have been completed on the Plynlimon surface waters by Neal & co-workers (e.g. Neal et al., 1986, 1990, 1992; Robson et al., 1990; Durand et al., 1994). Baseflow waters in the streams are typically of circum-neutral pH with relatively high Ca, Sr, Mg and HCO_3 , in contrast to more acid waters at high flows displaying high concentrations of Li, SO_4 , Y, Ba, Mn, Cu, Fe, Co, Al, DOC, NO_3 and B. The relationship between flow and concentration is variable depending largely on the antecedent conditions and in terms of rainfall amount and chemistry. Although chemical changes occur in the stream waters in relation to flow, the magnitude of these changes is significantly lower than expected from the change in water volume related to rainfall inputs. This is also the case for conservative parameters such as $\delta^{18}\text{O}$ and Cl (Neal & Rosier, 1990) and shows that the catchments have the ability to dampen or "buffer" the stream water chemistry.

These chemical variations were initially interpreted in terms of the mixing of different soil waters and rainfall. The upper soil zones are acidic and produce Al and transition metal rich solutions, whereas the lower mineral-rich zones produce relatively less acidic waters more enriched in base cations. The relative proportions of these waters were thought to be responsible for most of the variations found in the streams. The distinctive chemistry of baseflow waters and the use of hydrograph splitting techniques (Robson et al., 1990) indicated that an unidentified, relatively alkaline end member was largely responsible for controlling baseflow chemistry. The chemistry of the deeper soils appeared to be incompatible with the baseflow component and a project was set up to study potential deeper inputs to the catchment (Neal et al., 1997).

In order to assess the potential and significance of groundwater inputs to the catchment, a series of boreholes were drilled to different depths in the catchment. Groundwater was found in all boreholes and several indicated a significant volume of groundwater storage and flow (Neal et al., 1996). One of the deep boreholes (T 5) was drilled close to the Tanllwyth stream. During air rotary drilling the air supply was lost and a gas surge was seen to be erupting in the adjacent stream. The streamwater chemistry subsequently changed, with baseflow Ca and Sr showing four-fold increases in concentration. This indicated that the drilling had cleared a sealed fracture between the groundwater system and the stream. In addition, precipitation of iron oxyhydroxides occurred along seepages in the bedrock close to the stream and in the stream bed (Neal et al., 1996). The sources and pathways of solutes through the catchment are not well understood and detailed studies on both temporal and spatial chemical datasets are presently being studied in order to address some of these problems.

4.3 Sampling

A total of 45 water samples, including precipitation, soil porewaters, streams and groundwater from

boreholes were collected and analysed during this study. Two soil profiles (podzol and gley) were also studied in detail and representative samples of mudstone and greywacke and a vein assemblage from a disused mine sampled. Sample localities for the streams and boreholes are shown on Figure 4.2.

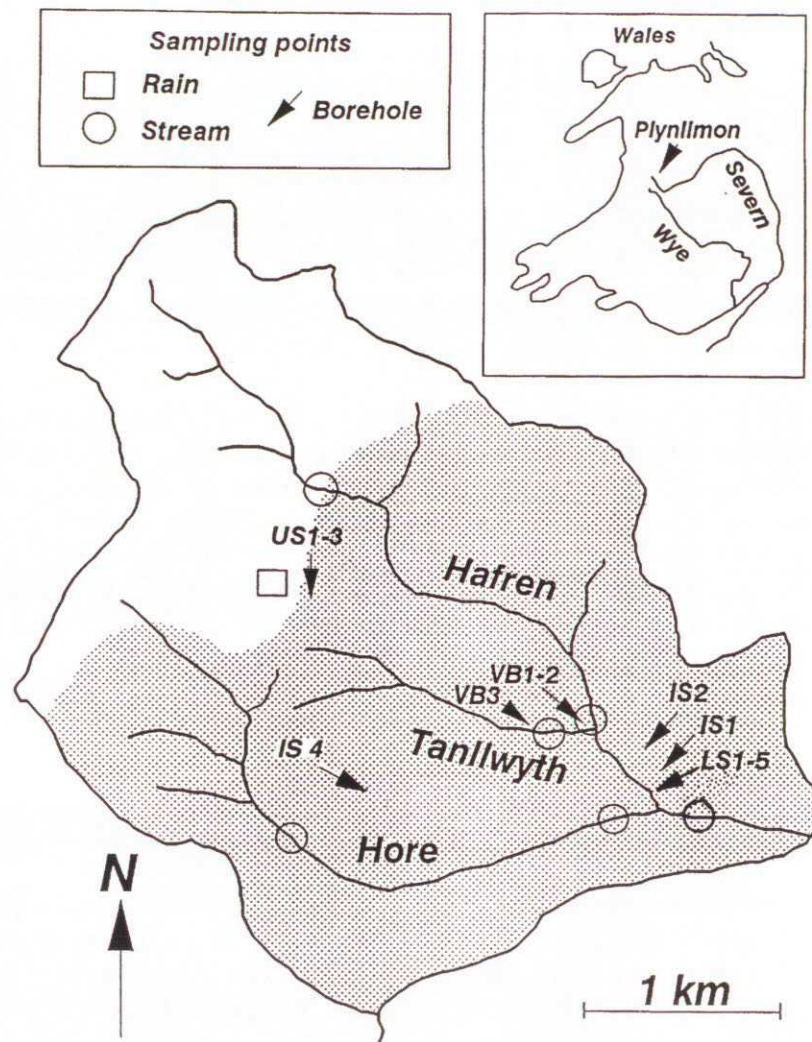


Figure 4.2 Map of the forested Plynllymon catchments showing locations of stream sampling sites, boreholes and meteorological site where rainfall was collected. Shaded area denotes forested areas.

4.3.1 Rock Samples

Although large reaches of the streams flow over bedrock, there is very little exposure on the interfluvies. Two samples of mudstone were collected from the lower and upper parts of the Hafren catchment. These are considered to be part of the Gestwyn shales and composed predominantly of illite with lesser chlorite and minor quartz and altered feldspar. A sample of grit was collected from a small quarry close to the edge of the forest in the upper reaches of the catchment. This sample was of variable grain size and composed dominantly of anhedral to subhedral quartz with lesser quantities of plagioclase and K-feldspar. The plagioclase feldspars showed various degrees of sericitisation and the K-feldspars were generally cloudy.

Chlorite is abundant, particularly along grain boundaries and rare patches of secondary calcite were present. A quartz carbonate vein from spoil tips at the Snowbrook mine in the Afon Hore catchment was also collected.

The rock samples were jaw-crushed and split, with representative 100-200g subsamples finely ground to give -200 mesh powder for isotope and geochemical analysis. The vein sample was coarse crushed and the carbonate fraction hand-picked under a microscope. Rb and Sr concentrations and Rb/Sr ratios were determined by X-ray fluorescence spectrometry (Analytical Geochemistry Group, British Geological Survey).

4.3.2 Soil Samples

Following a previous soil sampling exercise in November 1994, two soil profiles were sampled in the Hafren Forest in December 1995. The first profile was taken from a podzol in a relatively dense part of the forest, and the second from a gleysol excavated approximately 30 metres from the Nant Tanllwyth (Figure 4.2). These two soil types are believed to be the dominant soil types of the catchment. Sampling of the profiles was based on readily identifiable soil horizons. In order to keep the number of samples to a minimum, both profiles were split into three sections. For the podzol this comprised combining the humus layer with the dark brown organic-rich A horizon, and separating this from the brown B horizon and grey C horizon. The humus layer and the A horizon were also combined for the gley along with a narrow band of black peat. The distinction between the B and C horizons was less clear for the gley and the subdivision was somewhat arbitrary. The C horizon contained more bedrock clasts than the podzol and also demonstrated some characteristic mottling. Approximately 3-5 kg of soil per horizon were placed in sealed polythene bags, well mixed and stored at 4°C in a refrigerator prior to soil solution extraction and chemical analysis.

Pore water extraction

Soil solution was displaced from the field-moist samples within one day of sampling using the centrifuge drainage method (Kinniburgh & Miles, 1983). A Beckman J2-21 refrigerated centrifuge with a 6 x 250 cm³ JA14 fixed angle rotor was used. Specially made Delrin liners held the soil in the centrifuge rotor. All six liners were used for each horizon and were thoroughly washed in between. Operational settings were: speed, 14000 rpm (30000 g); temperature, 4°C; time, 35 minutes. Yields varied from 35% at the top of the podzol profile to 43% at the bottom and from 25% at the top of the gley to 52% at the bottom.

Mineral acid extraction

A previous study by Goody et al., 1995 used 0.43M HNO₃, 0.01M CaCl₂ and 0.1M Ba(NO₃)₂ to obtain a series of trace element partition coefficients for soils. The HNO₃ extraction releases both those metals adsorbed as cations and those present in readily-soluble oxide phases. The CaCl₂ extract is weaker in terms of acidity and ionic strength and does not dissolve the oxide phases significantly. The Ba(NO₃)₂ extract is similar to that of CaCl₂ but its higher cation concentration ensures a greater proportion of the exchangeable cations are displaced. The 0.43 N nitric acid extraction was chosen in the present study since it will remove exchangeable as well as sorbed and organically bound Sr (which may be an important potential source of Sr to the soil porewaters). The neutral salt extractants both contain Sr, which could be significant and difficult to correct for in a strontium isotope study. An early study using Sr isotopes on acid leachates of illite, montmorillonite and vermiculite showed that acid leaching only removed Sr from exchangeable sites (Chadhuri & Brookins, 1979). Goody et al. (1995) also found the 0.43M HNO₃ extraction the most simple for analytical determinations because the acid matrix (c. 3%) is quite similar to that used for the preservation of trace elements in water samples.

Approximately 10 g of air-dried soil from each horizon was accurately weighed into a pre-weighed 250 cm³ oak ridge polypropylene centrifuge tube to which was added 100 cm³ of 0.43 M HNO₃ (Suprapur7 grade, Merck). The tubes were shaken on a box shaker in a constant temperature laboratory (23°C) for 2 h, centrifuged for 10 min at 14 000 rpm, and finally the coloured supernatant solutions were filtered through 0.45 µm filter membranes. Extractions were performed in duplicate and for each horizon these were bulked. Approximately 100 ml of sample was collected for Sr isotope analysis and the remainder used for the determination of cations by ICP-OES and ICP-MS. A procedural blank was also prepared for isotope and cation analyses.

4.3.3 Water samples

a) Rainwater samples

Two rainwater samples were collected from the Carreg Wen Meteorological site at the headwater of the Afon Hafren (Fig 4.1). One-litre polyethylene bottles were used to collect two consecutive weekly rainfall samples between 26 September and 10 October 1995.

b) Stream and groundwater samples

Stream samples were collected from six sites (Figure 4.2) during December 1994 (stormflow), June 1995 (baseflow) and December 1995 (intermediate flow regime). Borehole samples were collected initially with a caravan pump and the boreholes were pumped for several minutes before sample collection and measurement. Only one very shallow borehole (US 1) at the headwater of the catchment was pumped dry. This borehole refilled relatively quickly and was sampled after being emptied several times. Depth samples were also collected during geophysical logging from the deep (VB2, VB3, LS6) and intermediate depth (US3 and IS4) boreholes. The depth samples were all collected during pumping except for the IS4 borehole which was sampled after completion of logging. It was realised that the pumped samples represented a mixed sample from several distinct fractures and that the chemistry was often dominated by higher TDS water from the deeper fractures. In order to preferentially sample water from shallowest fractures, waters were also collected using an open-ended bailer. The sample was collected after discarding five or more bailed volumes.

4.4 Analytical techniques and field measurements

On site analysis included temperature, specific electrical conductance (SEC), pH and dissolved oxygen (DO) by electrode (Figure 4.3) and total alkalinity (as HCO₃) by titration. With the exception of rainfall, all samples for laboratory analysis were filtered through 0.45 µm membranes. Filtered and acidified samples (1% v/v HNO₃) were collected in polyethylene bottles for major cation, SO₄ and a wide range of minor and trace elements by ICP-OES and ICP-MS. Calibrations for cation analyses were performed using appropriately diluted standards and both laboratory and international reference materials were used as checks of accuracy. Instrumental drift during ICP-MS analysis was corrected using In and Pt internal standards. Filtered unacidified samples for anion concentrations were analysed by automated colorimetry. Samples of unacidified and unfiltered water were collected in glass bottles for the stable isotopes ¹⁸O/¹⁶O and ²H/¹H and analysed on a VG Optima mass spectrometer. These are reported as δ-values relative to SMOW. Samples for Sr isotope analysis were filtered into nalgene bottles but not acidified in order to keep potential contamination to a minimum.

5 RESULTS

5.1 Bedrock samples

Whole rock $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the two mudstone samples are high (Table 5.1) and similar to Welsh Ordovician/Silurian mudstones presented elsewhere (Evans, 1996).

Sample	Rock type	Analysis type	Rb (ppm)	Sr (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$
PLR 1	mudstone	Whole rock	101	101	0.736980
PLR 1	mudstone	Illite fraction			0.736829
PLR 2	greywacke	Whole rock	32.4	47	0.723350
PLR 3	calcite vein	Whole rock	3.86	36	0.713533
PLR 3	calcite	Acetic acid extraction		-	0.711905
PLR 4	mudstone	Whole rock	151	106	0.736039

Table 5.1 Strontium isotope geochemistry of rock samples from the Plynlimon catchment.

The isotope ratio of the greywacke collected from near the headwaters of the Hafren catchment were significantly lower than the mudstone reflecting the relatively high plagioclase content. Strontium concentration is also lower reflecting the dominance of quartz. The vein sample from the spoil tips of the Snowbrook mine had the lowest whole rock isotopic ratio and a very low Sr concentration. The vein sample contained some host rock fragments, and an acetic acid extraction was carried out in order to determine the isotope ratio of the calcite. The calcite $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was significantly less than the whole rock value (Table 5.1).

5.2 Rainwater

The Sr isotope ratios of the two rainfall samples are indistinguishable within error from the values obtained for North Atlantic seawater (Table 5.2) and slightly lower than the range (0.7093-0.7104) reported by Bain & Bacon (1994) and Bacon and Bain (1995) from three sites in Scotland. The two samples collected were very different with respect to TDS: samples 1 and 2 had Cl concentrations of 13 and 1 mg l⁻¹ respectively. The long term Sr isotope ratio of precipitation is most likely to be similar to the measured values because of the dominant input into the catchment of a marine derived source for the alkali and alkali earth elements (Neal et al., 1997b).

Sample	Date	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr ($\mu\text{g l}^{-1}$)	Ca (mg l^{-1})	pH
Rainfall 1	26/9/95 – 2/10/95	0.709194	7.2	0.49	4.71
Rainfall 2	3/10/95 – 10/10/95	0.709178	1.3	0.08	5.37

Table 5.2 Strontium isotope and hydrochemical data for rainfall samples.



Figure 4.3 Measurement of pH, DO and Eh in groundwater in a flow through cell.

4.5 Separation of Strontium for Isotope Analysis

A suitable volume of each water sample, 10 to 200 ml depending on strontium concentration, was evaporated to dryness and the residue dissolved in 2.5 M hydrochloric acid. Aliquots of North Atlantic seawater were also prepared in the same way. Soil extraction samples were evaporated and the residue treated with 6 M hydrochloric acid. The solutions were then centrifuged and the supernatant liquid carefully decanted into nalgene beakers and evaporated. In some cases this procedure was repeated in order to obtain a clean solution when the residue was dissolved in 2.5 M hydrochloric acid. The whole rock samples were dissolved in a mixture of hydrofluoric and nitric acids (8:2) and, following evaporation, the residue was converted to the chloride form with 6 M hydrochloric acid. Strontium was separated from the water and rock samples by conventional ion exchange techniques using BioRad AG - 50W cation exchange resin. Strontium was loaded onto single tantalum filaments prepared with phosphoric acid, and isotope ratio measurements were made on an automated multicollector Finnegan-MAT 262 mass spectrometer. Data were collected over a period of two years and during that time the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for the NBS 987 strontium isotope standard varied from 0.710186 ± 0.000014 ($n = 14$) to 0.710244 ± 0.000011 ($n = 19$). Therefore, in order to be consistent, the measured isotope ratios have been normalised to a standard value of 0.710244.

5.3 Soil samples

The soil porewater and extraction data showed significant variations both in isotope ratio and element concentration in the profiles. (Tables 5.3 and 5.4). The isotope ratios and concentrations in the upper organic-rich O/A horizons are similar in both soil profiles and significantly above atmospheric $^{87}\text{Sr}/^{86}\text{Sr}$. The podzol shows a peak in Sr isotope ratio in the B-horizon in contrast to the gley where the ratio increases down the profile (Figure 5.1). Strontium concentrations correlate inversely with $^{87}\text{Sr}/^{86}\text{Sr}$ in the gley soil but there is little variation in Sr concentration in the podzol.

Soil and Horizon	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr ($\mu\text{g l}^{-1}$)	Ca (mg l^{-1})	pH (lab.)
Podzol O + A	0.711373	13.9	1.9	4.95
Podzol B	0.718964	12.5	1.7	4.81
Podzol C	0.714309	13.5	2.2	6.07
Gley O + A	0.711158	11.3	1.4	4.50
Gley B/C	0.712784	4.2	0.6	6.07
Gley C	0.713585	1.1	0.3	6.41

Table 5.3 Strontium isotope and geochemical data for soil porewaters.

The acid extractable Sr shows very similar trends to the porewaters but with much higher concentrations and higher $^{87}\text{Sr}/^{86}\text{Sr}$ (Table 5.4). The exception to this is $^{87}\text{Sr}/^{86}\text{Sr}$ of the O/A horizon in the gleyed soil where the ratio is slightly higher in the pore water. The porewater $^{87}\text{Sr}/^{86}\text{Sr}$ is thus not in isotopic equilibrium with the exchangeable $^{87}\text{Sr}/^{86}\text{Sr}$, however it displays similar trends through the soil profiles (Figure 5.5). The values of $\log K_d$ are generally similar in the organic horizons to data from acid sandy soils (Goody et al., 1995) but the C-mineral horizons have higher K_d values probably reflecting higher clay contents in the Plynlimon soils.

Soil and Horizon	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr ($\mu\text{g kg}^{-1}$)	Ca (mg kg^{-1})	$\log K_d$
Podzol O + A	0.712343	4110	339	2.47
Podzol B	0.740503	125	15	0.98
Podzol C	0.716174	770	105	1.74
Gley O + A	0.710545	1050	97	1.98
Gley B/C	0.715887	103	6.8	1.41
Gley C	0.727782	71	3.0	1.85

Table 5.4 Isotopic and geochemical data for 0.43 M HNO_3 soil extractions. $\log K_d$ is the log of the solid/liquid partition coefficient between the exchangeable Sr and porewater Sr.

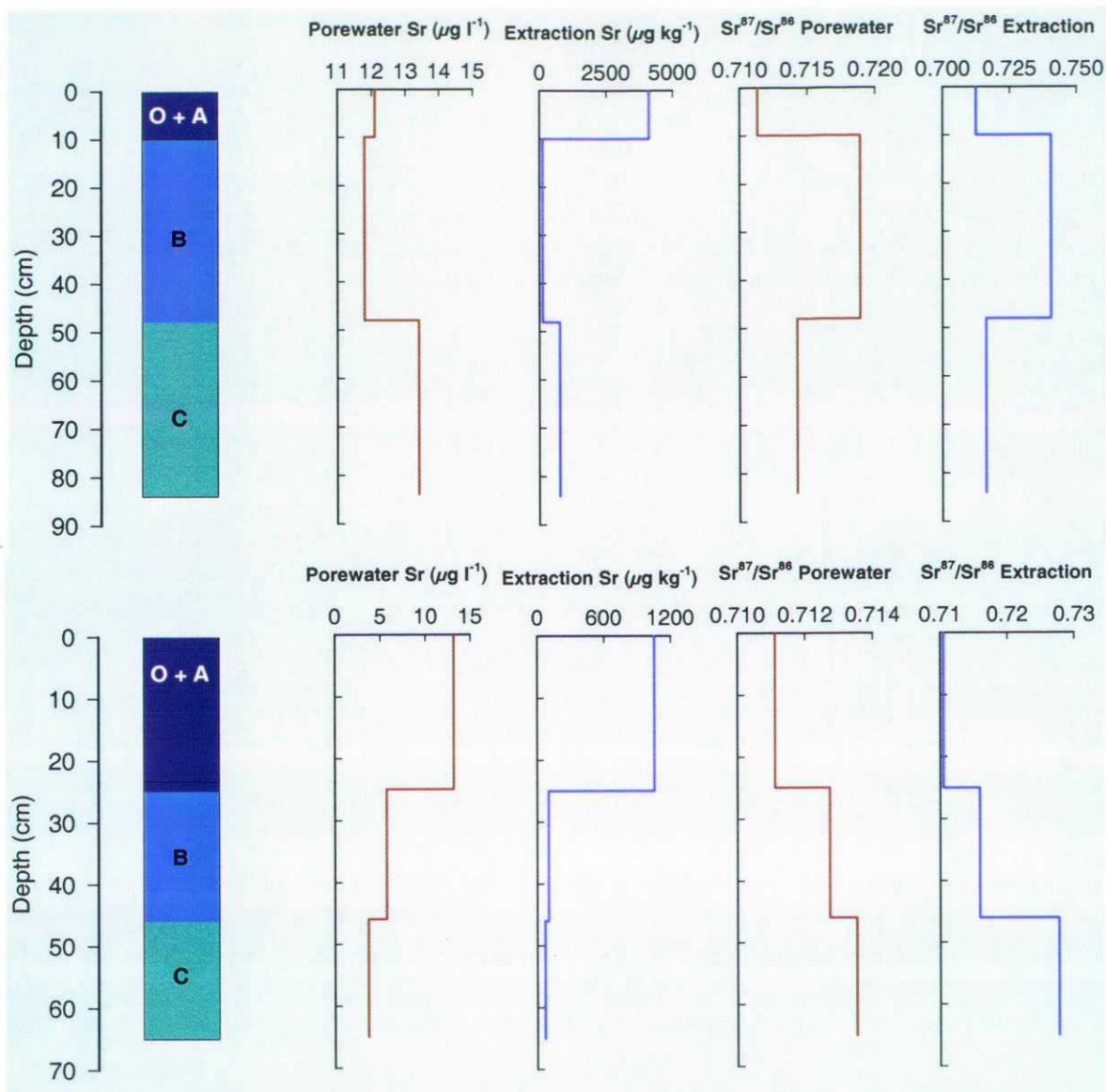


Figure 5.1 Porewater and exchangeable Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ in a podzol (top) and gley soil (bottom).

5.4 Streamwater samples

The stream water samples showed a significant variation in strontium isotope ratios between sites (Table 5.6) but relatively little variation during the different flow regimes. There was a significant decrease in Sr and Ca concentration with increased flow, but the magnitude of the decreases were much smaller than the changes in flow which showed an 12-20 fold increase at the four flume sites sampled (Figure 5.2).

Both the Afon Hafren and Afon Hore sub-catchments showed an increase in isotope ratio downstream from the upper sites, and both the Afon Hore samples were higher than the Hafren despite the presence of calcite (with a lower isotope ratio) in the headwaters of the former (Table 5.6). The Tanllwyth tributary is distinctive in its relatively high isotope ratio and Sr concentration and change in isotope ratio at high flow (Figure 5.2). The Severn sample represents the total outflow from the Plynlimon catchment and is intermediate between the three sub-catchments.

Sample	Site	Flow (cumecs)	Date	⁸⁷ Sr/ ⁸⁶ Sr	Sr (µg l ⁻¹)	Ca (mg l ⁻¹)	pH
PL1	Afon Hore (Flume)	0.0399	22/6/95	0.713408	6.1	2.2	6.63
		0.1027	5/12/95	0.713408	5.6	1.6	5.76
		0.7590	8/12/94	0.713110	3.7	0.8	4.79
PL2	Severn (Flume)	0.1233	22/6/95	0.713298	7.1	2.1	5.82
		0.2954	5/12/95	0.713206	6.4	1.5	5.65
		1.9576	8/12/94	0.712813	4.9	1.0	4.71
PL3	Afon Hafren (Flume)	0.0492	22/6/95	0.712351	5.3	1.1	6.78
		0.1371	5/12/95	0.712575	5.4	1.0	5.41
		0.5860	8/12/94	0.712290	4.7	0.59	4.67
PL4	Afon Hore Snowbrook	No flume	22/6/95	0.712581	5.0	2.6	6.31
			5/12/95	0.712649	4.6	1.8	5.86
			8/12/94	0.712426	3.4	0.55	4.62
PL95	Afon Hafren (Upper)	No flume	22/6/95	0.712023	4.7	0.78	6.51
			5/12/95	0.712024	4.8	0.67	5.60
			8/12/94	0.711586	4.0	0.48	4.67
PL98	Tanllwyth (Flume)	0.01433	22/6/95	0.714399	19.7	5.2	6.98
		0.02689	5/12/95	0.714018	11.2	2.6	5.90
		0.1830	8/12/94	0.713384	5.5	0.91	4.56
PL 98	Tanllwyth	0.0610	2/11/94	0.714478	19.5	5.12	6.95
PL 98	(older samples)	0.0660	7/2/92	0.713422	5.3	0.94	4.40

Table 5.5 Strontium isotope data for stream water samples (baseflow to stormflow shown in consecutive rows for each site).

5.5 Borehole samples

Strontium isotope data for the pumped groundwaters are presented in Table 5.6 and those from bailed samples in Table 5.7. There is a considerable range in isotope ratios varying from values similar to rainfall (0.709326) in the shallow borehole (US 1) at the head of the catchment to values approaching 0.715 in the deeper boreholes. The shallow pumped boreholes from the Hafren (LS 1, LS3), Carreg Wen (US 1, US 3) and the interfluvium (IS 4) showed a wide range in isotope ratios, whereas the Tanllwyth (VB 4) and nearby Met Site (VB 1) boreholes had consistently higher ratios. Depth samples were collected from the three deep (c. 45 m) boreholes (VB 3, VB 2, LS 6) during pumping and these all had relatively high ratios (Table 5.6) showing little variation with depth (Table 5.6). The pumped samples, however, showed an increasing trend when plotted against depth of borehole (Figure 5.3).

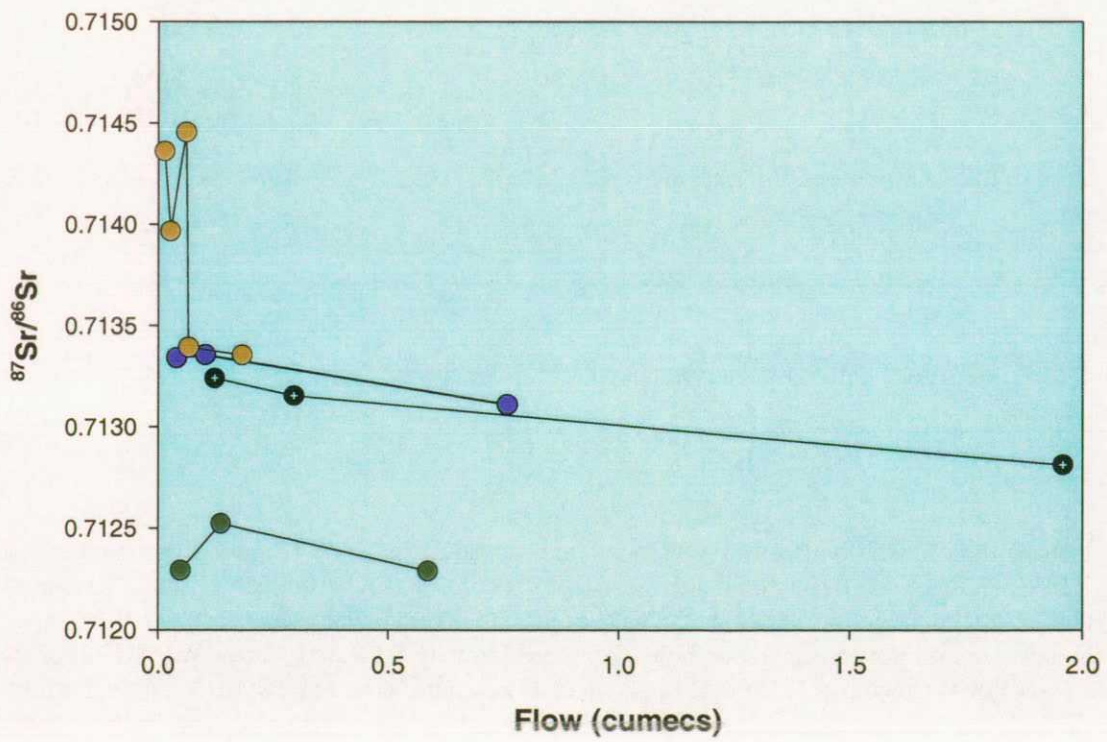
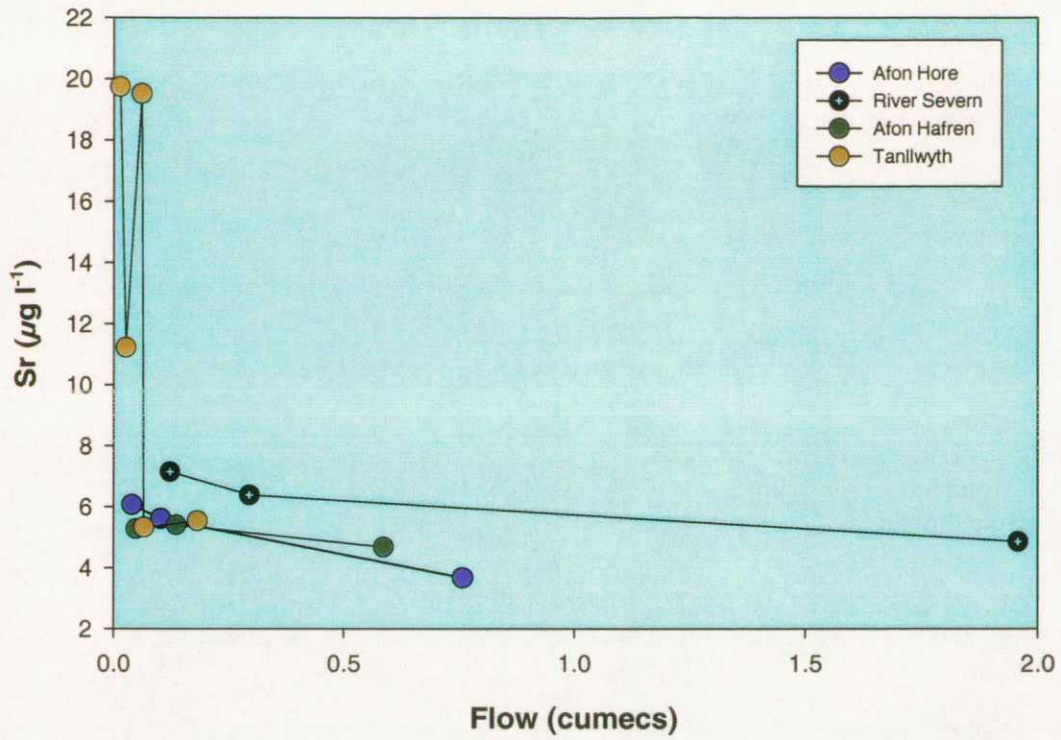


Figure 5.2 Changes in Sr concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ with flow in the Plynlimon streams.

Strontium concentrations showed considerable variation from values similar to those in streamwater in the shallow boreholes and headwater sites to greater than 300 $\mu\text{g l}^{-1}$ in the deep boreholes. Although the boreholes show a general increase in Sr concentration with depth (Figure 5.4), Sr isotope ratios remain relatively constant and significantly less than the dominant host rocks of the catchment.

Borehole number	Borehole depth (m)	Sample depth (m)	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr ($\mu\text{g l}^{-1}$)	Ca (mg l^{-1})		
US 1	2.70	Pumped	0.709326	11.9	3.1		
US 3	14.10	pumped	0.710951	11.3	2.0		
LS 1	6.40	pumped	0.712591	12.8	3.1		
LS 3	8.00	pumped	0.710995	9.6	2.9		
LS 6	44.50	pumped	0.714597	114	21		
		12	0.714361	120	22		
		24	0.714604	132	23		
		29	0.714604	149	23		
IS 1	10.20	pumped	0.711231	55	10		
VB 1	11.00	pumped	0.715211	35	9.3		
VB 2	47.40	pumped	0.714621	56	14		
		7	0.714477	250	58		
		12	0.714339	320	72		
		16	0.714195	341	77		
		20	0.714054	346	81		
VB 2	47.40	40	0.714900	263	58		
		VB 3a	7.00	pumped	0.714943	44	14
		VB 3	44.40	pumped	0.714889	110	29
7	0.714726			153	39		
9	0.714832			178	46		
16	0.714792			187	49		
27	0.714776			189	50		
38	0.714745			332	67		
IS 4	27.50	18	0.713006	33	26		
		23	0.713444	31	29		

Table 5.6 Strontium isotope data and geochemistry of pumped and depth samples from boreholes.

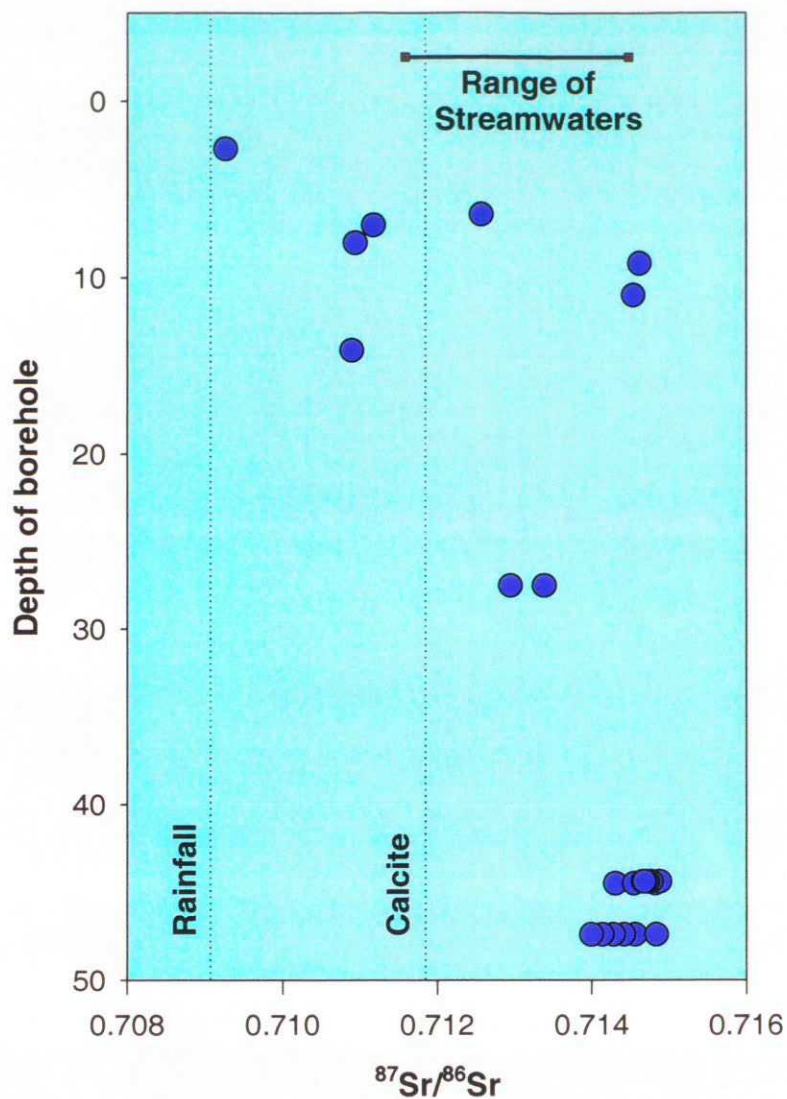


Figure 5.3 Plot of $^{87}\text{Sr}/^{86}\text{Sr}$ vs. depth of borehole showing general increase in the isotope ratio with depth.

Borehole number	Borehole depth (m)	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr ($\mu\text{g l}^{-1}$)	Ca (mg l^{-1})
IS 1	10.2	0.713959	5.3	1.77
LS 4	11	0.712638	8.1	2.01
LS 3	8	0.712626	6.6	1.09
LS 1	6.4	0.712591	6.1	1.33
VB 1	11	0.715211	7.9	1.67
VB 3	16	0.717622	6.5	1.41
IS 3	8.5	0.711757	4.9	1.49
US 1	2.7	0.710377	5.5	0.60

Table 5.7 Strontium isotope data and geochemistry of bailed samples from selected boreholes.

6 STRONTIUM ISOTOPES AS AN INDICATOR OF FLOW IN THE CATCHMENT

6.1 Introduction

Strontium isotopes are not fractionated by low temperature geochemical processes or by biological processes, and therefore can yield information about the sources of strontium and the flow and transfer of strontium within an ecosystem. The variations in strontium concentration related to changes in discharge are difficult to interpret due to the large number of potential sources e.g. atmospheric, weathering, decay of organic matter and from ion exchange sites in the various soil horizons. Although the acid soil porewaters are lower in base cations than at least some of the baseflow stream waters, there is considerable storage in the ion-exchange pool. In addition, the low pH and high aluminium and organic carbon found during high flow indicates that the upper soils are important in contributing solutes to the streams.

Graustein (1989) concluded that much of the Sr in runoff was not derived from soil solution. He considered two possibilities to explain low Sr isotope ratios in soils studied compared with runoff: 1) most of the flow from the soil surface to the aquifer occurred by rapid transport or 2) strontium in the shallow soil solution was totally absorbed in the rooting zone and replaced by weathered strontium below the root zone. These conclusions cause problems for relating flux information and budgets in soil zones to nutrient budgets derived from stream hydrochemical data (Graustein, 1989). The importance of ephemeral natural soil pipes between the organic and mineral horizons in contributing to stormflow was considered by Chapman et al. (1993) during a study of the adjacent, unforested Plynlimon Wye catchment. As discussed previously, the baseflow chemistry is difficult to interpret in terms of soil chemistry and a component of groundwater has been considered to be a significant contributor to streamflow generation, at least at baseflow.

Sklash et al. (1996), using stable isotope signatures in the adjacent Wye catchments, showed that pipe flow during stream baseflow and stormflow was dominated by "old" groundwater discharge, but rainfall influenced the isotopic and chemical character of the groundwater. The storage capacity of the catchments was also suggested to be significant. The groundwater component in the streams was considered to be well mixed, however it was suggested that two "old" components were present: an up slope groundwater transported via ephemeral pipes and a near stream well-mixed old water controlled by Darcian flow. Although little data was available for soil waters, their influence was thought to be minimal as the data could be explained by mixing of the above components.

This section first describes the variation in each of the different catchment units studied and then tries to relate these to the variations found in the streamwaters in order to constrain the dominant mixing processes involved in streamflow generation.

6.2 Soils

The soil horizons show a wide range in both Sr concentrations and isotope ratios (Figure 5.6). In the gley profiles (Figure 5.6 b), Sr concentrations show a decrease in concentration with depth in both porewaters and in the exchange pool, whereas Sr isotope ratios show an increase. The porewater Sr isotope ratios are intermediate between the exchangeable Sr and that derived from rainfall and are interpreted as mixing between these two components. The fact that the porewaters are not in isotopic equilibrium with the exchange pool, demonstrates inefficient exchange during water transport through the soils, most likely due to rapid transit rates through the soils or to the unavailability of the exchange of Sr because of discrete flowpaths or to Sr being present in unreactive sites. The high Sr in the exchange complex of the upper

organic-rich soils is related to nutrient cycling and release from biomass. This Sr is dominantly atmospheric-derived but a small component of weathering-derived Sr is present. This profile is considered to be typical of a simple weathering profile where active weathering is occurring in the deeper parts of the soil zone in the C horizon.

The podzol profile also displays some of the characteristics displayed by the gley, but very high Sr isotope ratios are present in the B horizon, as well as very low Sr concentrations in the exchange pool. This implies weathering of a radiogenic component of soils, most likely illite or chlorite which swamps the Sr of atmospheric derivation.

The soils, therefore, show significant vertical heterogeneity, but the deeper weathering horizons of both soils are similar. It is clear that contributions from the organic soil horizons are easily discriminated from the deeper mineral soil horizons and it is likely that mixing between porewaters from the different soil horizons would produce significant variation if they form a major component of streamwaters.

6.3 Streams

There is significant overall variation in both the strontium concentration and isotope ratios in the streamwaters. Solute strontium in the streams represents a mixture of atmospheric-derived strontium and that derived from weathering. Strontium concentrations at individual sites show a typical decrease in concentration with flow but this is small in comparison with the large increases in discharge. Strontium isotope ratios at individual sites show a remarkably small change in isotope ratio except for samples in the small Tanllwyth tributary. This lack of variation implies a well mixed relatively homogeneous source of Sr. Isotope ratios in the Afon Hore and Afon Hafren increase downstream implying a greater proportion of atmospherically-derived Sr in the headwaters with weathering-derived Sr becoming more important downstream. The larger variations over the catchment as a whole show that local well mixed discrete sources are present.

The Tanllwyth tributary shows the largest variation both in terms of strontium concentration and isotope ratio. The dominant soils in the Tanllwyth are gley soils composed of c. 1 m thick grey impermeable clays and it is likely that throughflow or overland flow may be important following large rainfall events which may cause significant dilution. During the drilling of one of the deep Tanllwyth boreholes (VB 3), air flush was lost and the Tanllwyth stream began to bubble furiously. It was likely that a sealed fracture had thus become cleared which was in contact with the stream. Following this, baseflow Ca and Sr increased five-fold. Unfortunately, it was not possible to analyse pre-drilling samples for strontium isotopes although stormflow samples showed no change in samples collected prior to drilling.

6.4 Groundwater

The groundwaters in the Plynlimon catchment have a wide range of strontium isotope ratio and concentration. Depth samples from the deep boreholes show that relatively evolved groundwaters are present at depth and the high strontium concentrations compared to rainfall and soil porewaters shows that the dominant source of strontium is from weathering of bedrock in the groundwater environment. Lower strontium concentrations were present in the shallowest depth samples but these samples probably have a significant component derived from deeper fractures and it was not possible to determine the concentration or ratios directly from shallow fractures. These deeper groundwaters displayed a distinct maxima in the isotope ratio implying a discrete mineralogical control (Figure 6.1). The source of this strontium will be discussed in section 7. Groundwaters in the headwaters of the catchment display the least radiogenic strontium isotope ratios with one very shallow groundwater having a ratio only slightly higher than rainfall.

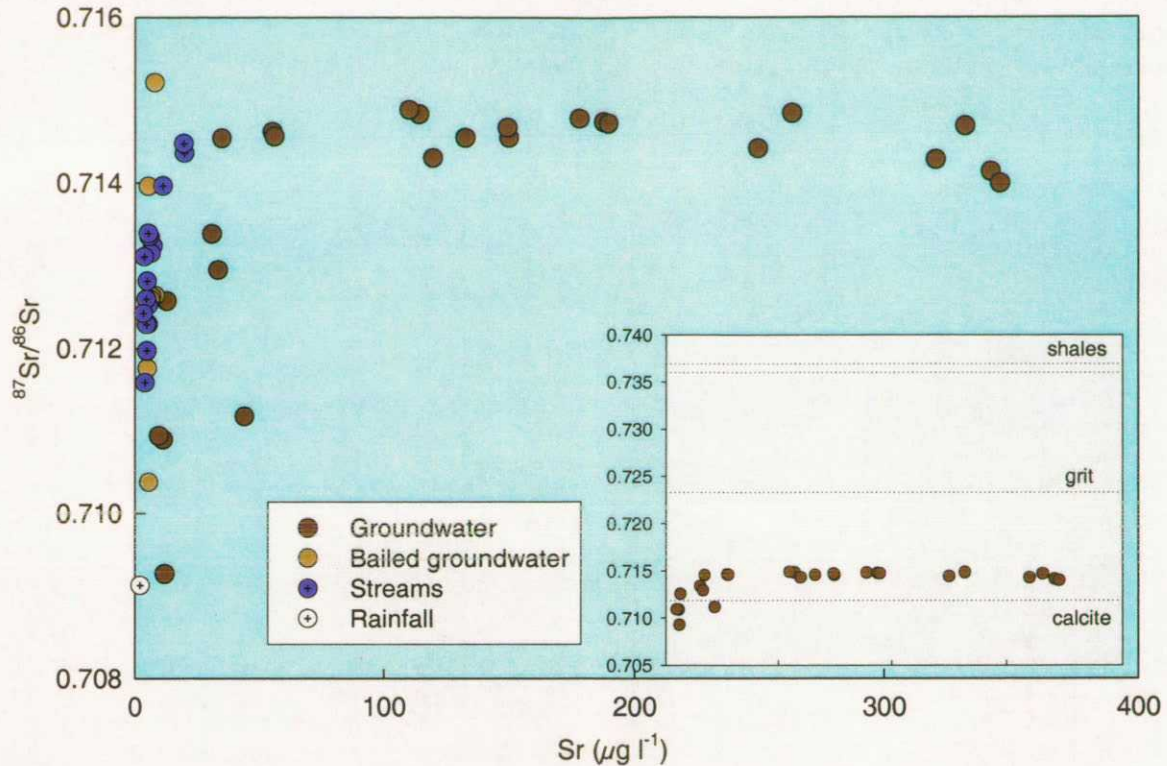


Figure 6.1 Plot of Sr vs. $^{87}\text{Sr}/^{86}\text{Sr}$ in Plynlimon waters illustrating a clear maxima in isotope ratio.

It was not possible to isolate individual inputs of flow to the borehole, however, geophysical logging showed that deep and shallow inflows were present. The groundwaters in these deep boreholes also showed significant chemical variations with depth (Figure 6.2). Although the pumped discharge concentrations were much lower, the precise chemistry of the shallow fractures could not be ascertained because these represent mixtures of both shallow and deep groundwaters. In order to preferentially sample water derived from shallow fractures, samples were collected using a plastic bailer: the first five or more samples were discarded to avoid sampling any stagnant water, which might have been present in the borehole casing. The bailed samples had much lower strontium concentrations than the pumped samples with both concentrations and isotope ratios being generally similar to the stream waters. One bailed sample had a very high isotope ratio close to that of the B horizon porewaters of the podzol soil.

6.5 Catchment mixing processes and streamflow generation

Strontium is not fractionated by low temperature geochemical or biochemical processes and can, therefore, be used to indicate the potential components of mixing. Strontium isotope ratio is plotted against $1000/\text{Sr}$ for the Hafren and Tanllwyth sites, where most data are available, in Figure 6.3. This plot is useful because the mixing of two components is represented by a straight line between the two components. This clearly has potential to constrain models for the evolution of streamwaters: it will indicate whether two or more end members are present and the feasibility of the several potential components in the system. The small change in isotope ratios in the streams implies a well-mixed source and the potential inputs can be discussed with reference to the mixing diagram (Figure 6.3). Some of the shallow groundwaters lie close to the upper organic soils but most form a tight cluster. It is evident that the streamwaters do not lie on a mixing line between the upper and lower soil horizons or between the soils and groundwater. In the case of the Hafren, the stream waters lie on a mixing line between the groundwater or deep soil and average

rainfall, and in the Tanllwyth, between groundwater and average rainfall. Only in the case of the Tanllwyth, which shows the largest change in concentration with flow, is there a shift away from this line. The Tanllwyth stormflow stream waters, however trend towards the deeper soils and not the shallow organic horizons as expected.

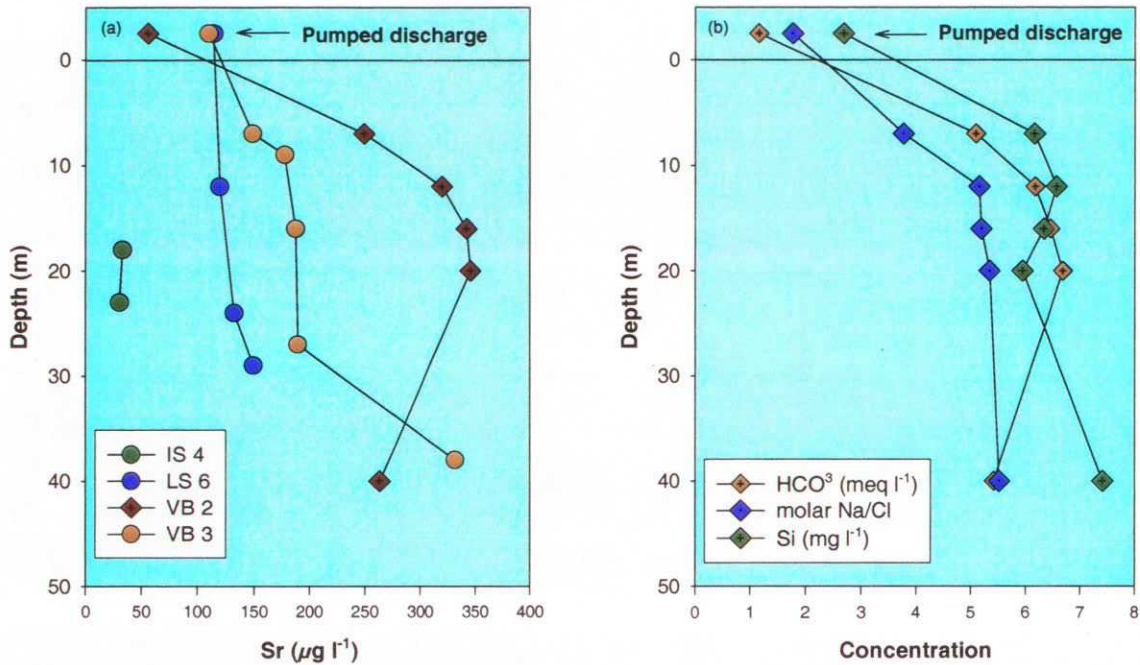


Figure 6.2 Depth variations in groundwater samples collected during pumping for (a) Sr concentration in boreholes and (b) bicarbonate, molar sodium/chloride ratio and silicon.

A plot of $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $1000/\text{Sr}$ is shown for all the data on Figure 6.4. Most of the pumped groundwaters form a tight cluster with relatively high strontium concentrations and isotope ratios; this cluster is dominated by groundwaters situated close to the valley bottoms. The Sr in these boreholes is dominated by strontium derived from weathering of bedrock. Several pumped samples, those in the headwaters and interfluvial area, lie close to the upper organic soils or on a mixing line between the upper soils and groundwater showing that soil inputs are important to the shallow groundwater in these areas. The samples which fall below or to the left of this mixing line have most likely been strongly affected by evapotranspiration processes, which affect the concentration but not the isotope ratio. The majority of the bailed samples lie on a mixing line between rainfall and the deeper groundwaters implying that the water derived from these shallow fractures is formed by dilution of the more evolved deeper groundwater. Taking into account the strontium concentrations and position on the mixing diagram, it appears that the deeper weathering parts of the soils do not form the major input to the groundwater system. The differences between the deep and shallow groundwaters show that mixing is not rapid and probably takes place along discrete fractures connecting the two, but they are largely not in hydraulic continuity. The difference in the concentrations of strontium between the bailed samples and the deeper groundwaters indicates that very small amounts of the evolved groundwater are present in the shallow groundwater, but this has proved difficult to prove due to sampling difficulties in deep open hole boreholes. Ideally, therefore, sampling should be completed either using packers or from sealed depth-specific boreholes.

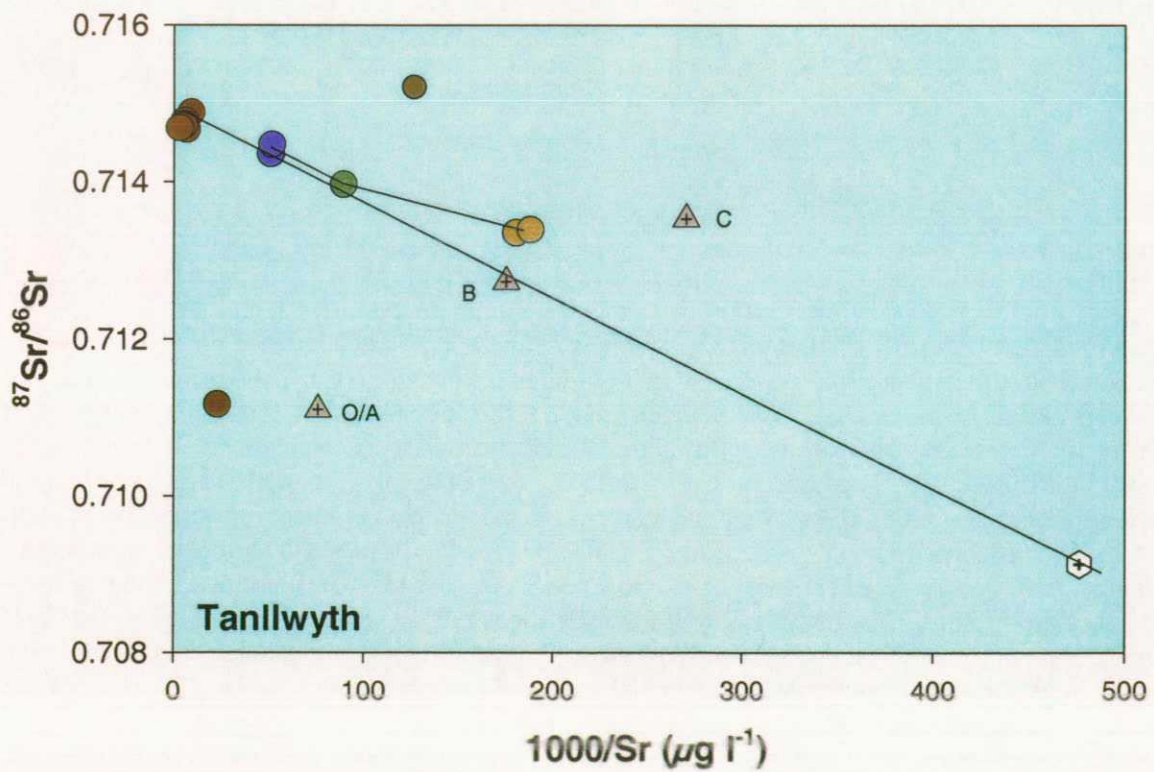
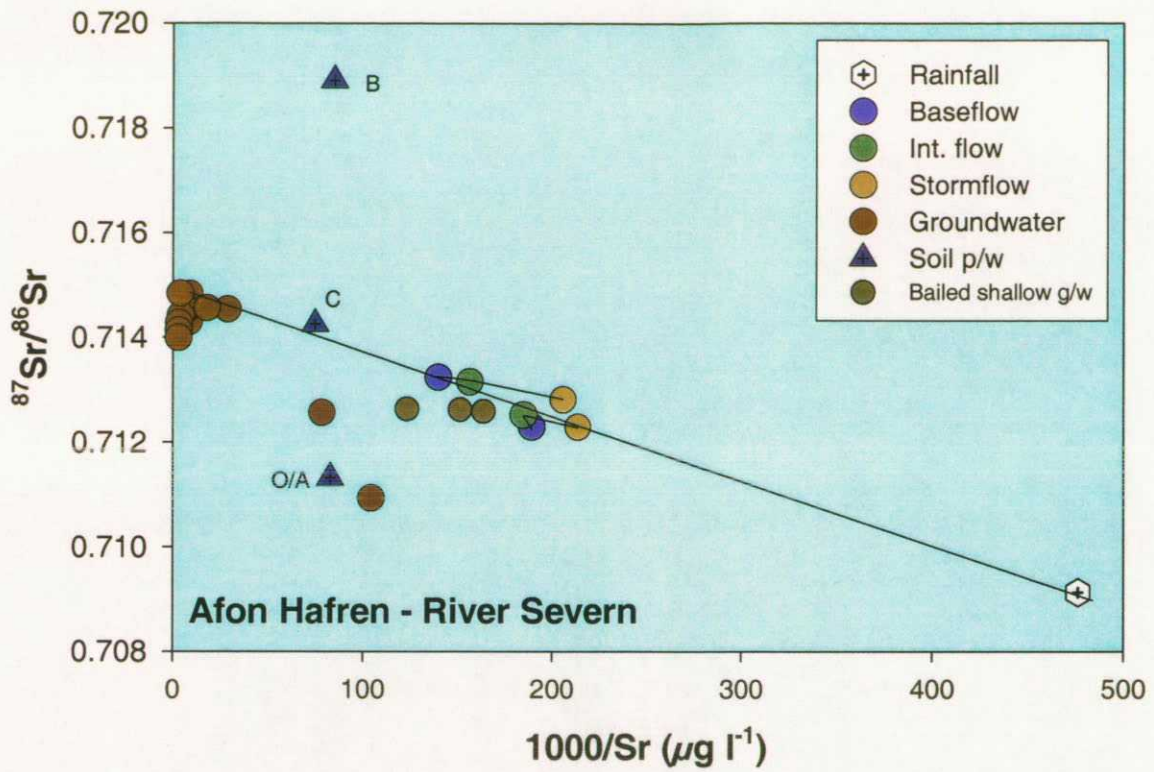


Figure 6.3 Plot of $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $1000/\text{Sr}$ for the Hafren and Tanllwyth sites. Soils are annotated with the horizon from which the porewaters were extracted.

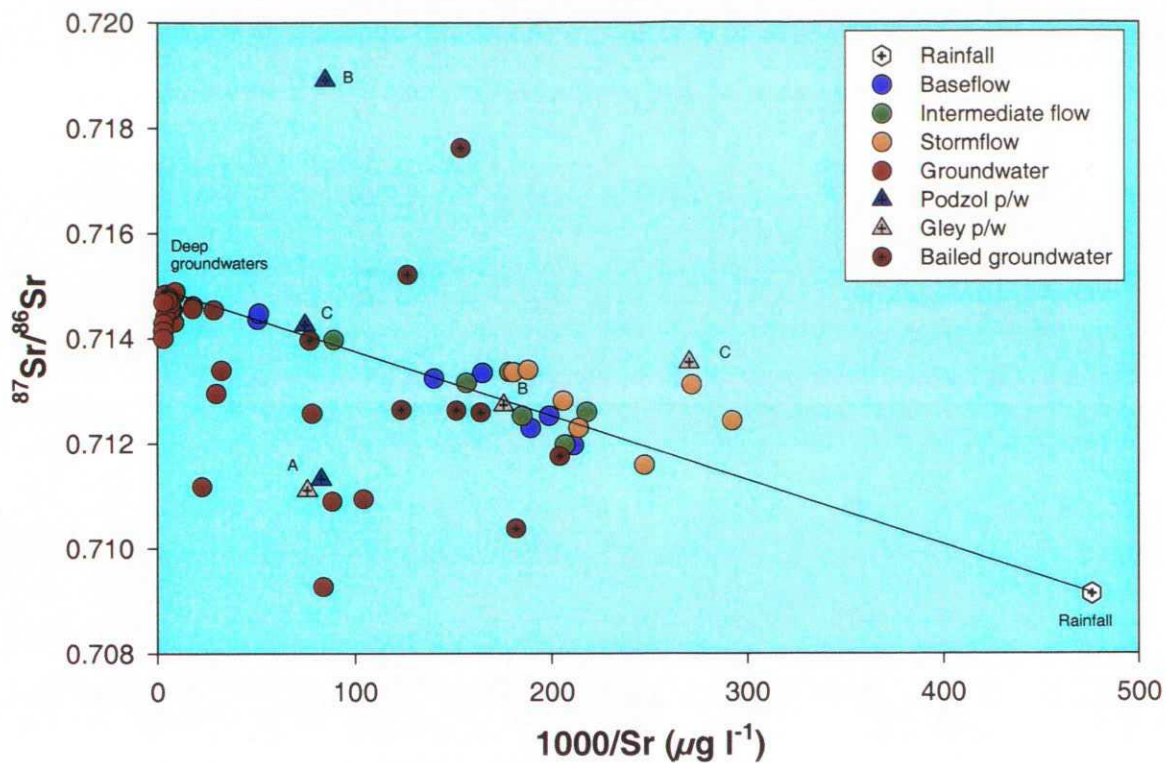


Figure 6.4 Plot of $1000/Sr$ vs. $^{87}Sr/^{86}Sr$ in Plynlimon samples. The solid line represents a mixing line between average rainfall and intermediate-deep groundwater in the catchment. Most stream samples fall on such a mixing line and trend away from the upper soil porewaters during stormflow. Note the similarity of some of the bailed groundwater samples to the streams.

The stream water data lie dominantly on a mixing line between rainfall and the deeper groundwaters implying that these components form the major inputs to the streams (Figure 6.4). Although the C horizon podzol porewaters also lie on this line and represent the dominant soils of the catchments it is considered that these do not represent the dominant influence at least during conditions: the soils are generally too acidic and alkalinity too low. The trend during higher flow conditions is away from the porewaters towards lower strontium concentrations; however, dilution of the podzol soil porewaters may occur during storm events and this would generally be towards the rainfall component. It is considered unlikely that dilution of the porewaters and mixing with rainfall would lead to such homogeneity as found in the streamwaters at different flow conditions. The variation in the amount of dilution, the short term variation in strontium concentration of the rainfall and variation in ion exchange processes during percolation implies that such a scenario should produce significant variation. It is clear that the source of the dominant input is relatively well buffered for most of the flow conditions and together with the fact that shallow groundwaters are so similar in terms of isotope ratio and concentration to the streams may imply that there is a dominant input from the shallow groundwaters to the streams. This would indicate that flow routing through bedrock fractures is important for the transfer of rainfall to the stream channel. The results from geophysical logging are consistent with this conclusion: both shallow and deep inflows were found with the shallow groundwaters (< 10 m) having a significantly lower temperature and SEC (Figure 6.5). The higher SEC at depth is also consistent with the conclusion that there is limited contact between the deeper bedrock groundwaters and the shallow system or stream.

organic loadings which indicates an important role for the soils in streamflow generation. It has been noted during rainfall events that many of the boreholes close to the stream become artesian due to rapidly rising water tables and this explains the flashy nature of the streams following rainfall. This also shows that the groundwaters rise into the soil horizons and reaction between the groundwater and soils occurs. It is considered that during this stage many of the soil inputs to stormflow, such as lower pH and higher Al and organic carbon, takes place.

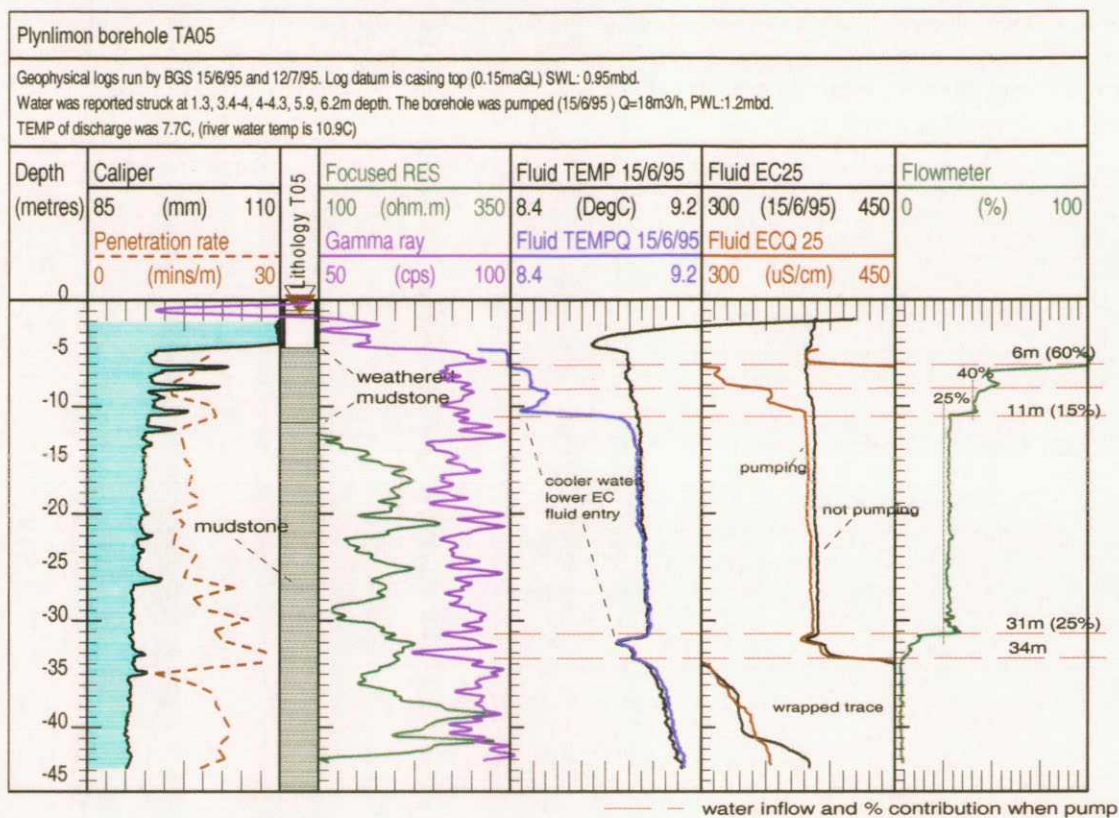


Figure 6.5 Geophysical log of borehole VB 3 (TA05) close to the Tanllwyth stream.

The fact that there is such a small variation in isotope ratios in the streams is taken as evidence that the stream water cannot be a recent mixture of rainfall and deep groundwater because it is unlikely that this could produce a relatively constant isotope ratio: during large rainfall events the streams would be dominated by rainfall and at baseflow by groundwater, which should result in large temporal variations in the isotope ratios measured in the streams. The evidence indicates that the source is well mixed implying a significant residence time and storage in the shallow bedrock fractures. This model is also indicated by the recent stable isotope studies (Sklash et al., 1996) which showed that the dominant input to streams in the adjacent Wye catchment is dominated by older pre-event groundwater.

The water table in the Plynlimon catchments fluctuates rapidly following rainfall events and it is concluded that most of the increase in flow is due to the displacement of relatively "old" pre-event water. The rapid response of the streams to rainfall inputs is simply due to the fact that the catchment is able to transmit changes in hydraulic gradient which occur rapidly compared with water transport. There is, therefore, a decoupling between the physical and chemical parameters. The dilution of many solutes during large rainfall events does indicate that dilution from rainfall occurs, but this is considered to be a relatively small direct input as indicated by the buffering of the solutes in comparison to the very large increases in flow. Recent rainfall is transported through the catchment whilst undergoing reaction and mixing in the bedrock system. Simple mixing calculations show that the amount of deeper groundwater incorporated into the streams during mixing is very small (a few per cent) due to the high strontium concentrations present at depth.

This model explains the apparent buffering capacity of catchments in terms of the damped response of many solutes, but fails to explain the large increase in acidity, aluminium concentrations and stream

organic loadings which indicates an important role for the soils in streamflow generation. It has been noted during rainfall events that many of the boreholes close to the stream become artesian due to rapidly rising water tables and this explains the flashy nature of the streams following rainfall. This also shows that the groundwaters rise into the soil horizons and reaction between the groundwater and soils occurs. It is considered that during this stage many of the soil inputs to stormflow, such as lower pH and higher Al and organic carbon, takes place.

7. STRONTIUM ISOTOPES AS INDICATORS OF CHEMICAL WEATHERING AND WEATHERING RATES

7.1 Introduction

Chemical weathering is the term used to describe the transformation of minerals formed at particular P-T conditions within the earth into more stable secondary minerals and solute species through interaction with dilute waters close to the earth's surface. Weathering of carbonate minerals is generally rapid in comparison with much slower rates for silicates, and although much less abundant in terms of quantity, provides a disproportionate input into natural waters. The weathering of silicate minerals is important because the release of base cations to solution provides plant nutrients as well as neutralising acidity and generating alkalinity (Drever, 1997). The role of silicate weathering is also considered to be an important control on atmospheric CO₂ and consequently important in studies on greenhouse warming. Unlike carbonate weathering where CO₂ consumed in dissolution, is released during precipitation of calcite in the oceans, silicate weathering and subsequent precipitation results in a net loss of CO₂ from the earth's surface (Walker et al., 1981; Berner et al., 1983). This makes estimates of weathering rates important in predicting the effects of climate change at both a local and worldwide scale. The rates of chemical weathering are also important to establish in catchments in order to effectively model changes imposed e.g. by land-use change and soil acidification related to acid rain. The soil zone, where weathering is intense, has traditionally been considered as dominating weathering and the export of solutes from catchments. However, the export of solutes may be derived from less intense weathering of large volumes of rock in the sub-surface environment. It is evident from geochemical studies of soils and groundwater that both are important, but the relative importance of each is not well established.

Chemical weathering results in the production of base cations and alkalinity from reactions between rainfall and soil-derived carbonic acid with solid phases as discussed in section 1.3. This supply of base cations is augmented by input from atmospheric deposition, and in order to calculate weathering rates it is necessary to calculate the inputs of this deposition. The rate of weathering determines the response and long-term resistance of the catchment to acidification (or several other forms of pollution). The weathering of silicate minerals is extremely important because silicate weathering reactions are generally non-reversible and therefore act as a long-term sink of H⁺. Ion exchange reactions, on the other hand, are rapid and reversible and may only act as temporary sinks to acidity. This section attempts to ascertain 1) where in the Plynlimon catchment weathering occurs, and 2) chemical rates of weathering based on a combination of Sr isotopes and long term flux measurements of rainfall and stream solute-flux from the catchments.

7.2 Weathering in the Plynlimon catchment as indicated by ⁸⁷Sr/⁸⁶Sr

Previous studies of weathering in the Plynlimon catchments have concentrated on XRD studies of weathering phases in soils or on mass balance studies (Durand et al., 1994). This section will deal with weathering processes in the soils and groundwater environment and estimation of weathering rates for Sr and Ca based on a mixing model between weathering- and atmospheric-derived Sr. The mobility and behaviour of Sr during weathering processes are controlled by competition between the leaching of primary minerals and adsorption through cation exchange reactions onto secondary products and clay minerals (Nesbitt et al., 1980).

Most catchment weathering studies have concentrated on areas where bedrock mineralogy is relatively simple (typically coarse grained igneous and metamorphic rocks) and where knowledge of the dominant weathering reactions and products is well established (Drever & Clow, 1995; White & Blum, 1995).

Characterising the dominant minerals and weathering reactions in catchments dominated by fine grained rocks such as found at Plynlimon is extremely difficult. The soil mineralogy at Plynlimon is related to the bedrock but with alteration of chlorite and transformation of illite to vermiculite. Chlorite is relatively rare in the upper soils but increases with depth in contrast to vermiculite which is high in the upper parts of the soils (Hornung et al., 1986). Although carbonate is present in vein mineralisation in the Upper Hore, it appears to be absent from the soils and mudstones of the Hafren catchment. The Sr isotope data are summarised as ranges on Figure 7.1.

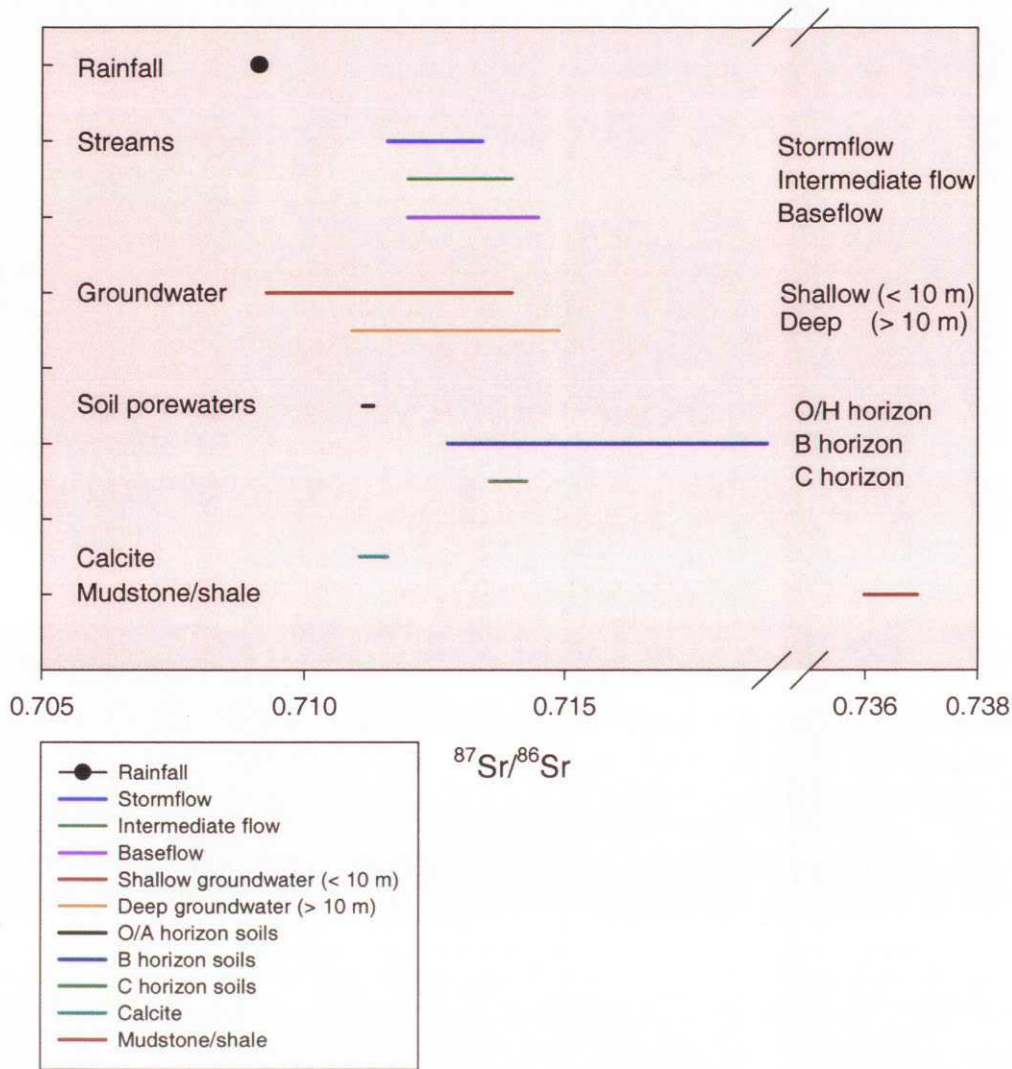


Figure 7.1 Summary of Sr isotope data for the Plynlimon catchment.

7.2.1 Weathering in the Plynlimon soils

The soil profiles of the podzol and the gley shown in Figure 5.1 provide evidence for significant vertical heterogeneity. The Sr isotope ratios in the porewaters lie between the Sr isotope ratio of rainfall and the exchangeable ratio and represent incomplete mixing between these sources. The upper organic horizons are dominated by atmospherically-derived Sr, and the isotope ratio generally increases with depth to the

mineral C-horizon soils. The exception is the B-horizon of the podzol, which has very high ratios indicating intense weathering. This is most likely a consequence of intense leaching of sheet silicates related to proton production during podzolisation. The exchangeable Sr, however, is much lower than the upper and lower horizons. There is a negative correlation between Sr isotope ratio and concentration with high concentrations in the organic-rich horizons controlled by biomass recycling and decomposition of organic matter. As mentioned previously, the variation in weathering rates of minerals generally leads to the weathering Sr having a different isotopic ratio to the whole rock or soil. Radiogenic strontium is usually contained in the more stable (K, Rb-rich) phases generally the finer grained fraction of soils (Brass, 1975). The maximum ratios in most of the profiles indicate that the weathered Sr has an isotopic ratio significantly less than that of the whole rock value. This may indicate mixing with atmospheric Sr or input from a component less radiogenic than the illite/chlorite which dominate the mineralogy of the whole rock and will be discussed later.

The three main considerations applied to estimating soil weathering include residence time of the porewater, preferential mobilisation from minerals, and isotopic disequilibrium between the soil exchange sites and porewaters. The Sr isotope ratio of the weathering end-member is often considered to be that in the exchange pool of the weathering C-horizon. Solid phase soil extracts, however, are not truly end-members in the sense that they themselves may be mixtures of atmospheric and weathering-derived. Previous approaches have used ammonium acetate extracts or salicylic acid leachates from soils to represent the weathering end-member composition (Åberg et al., 1987; 1989; Wickman & Jacks, 1991). This study has chosen a weak inorganic acid, which represents a stronger extractant but one which mobilises most of the Sr bound to soil minerals. The soil porewaters are not in isotopic equilibrium with the nitric acid extractions, a case previously noted by Bullen (1995) comparing soil porewater Sr to exchangeable Sr. Some of the exchange pool Sr in this previous study was considered to be from the previous release of radiogenic strontium from reactive minerals e.g. biotite, during an earlier stage of weathering following glaciation. It is thought more likely for the Plynlimon soils that the disequilibrium is due to the inefficient exchange or mixing of porewater Sr with exchange sites in the soil or to rapid transit times of bulk precipitation through the soils. The effect of previous weathering regimes e.g. following glaciation is difficult to estimate based on the limited Sr isotope data and knowledge of the age of the soils.

The variability of weathering in soils across the catchment is difficult to estimate but likely to be variable from the upper to the lower slopes. Previous studies (BGS, unpublished data) of soil profiles from close to those sampled in this study here indicate little local variation.

7.2.2 Weathering in the Plynlimon catchment groundwater system

The shallow groundwaters are variable both in terms of Sr concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ but there is a general increase in Sr in the shallower groundwaters, up to c. $30 \mu\text{g l}^{-1}$ Sr. The deeper groundwaters show large increases in Sr concentration (up to $346 \mu\text{g l}^{-1}$) but with no further increase above a maximum of c. 0.7148 (Figure 6.1). This implies that the isotope ratios are being controlled by a single mineral phase and not a mixture of phases. This ratio is significantly higher than calcite sampled from the upper Hore and much lower than the whole rock which is dominated by the sheet silicates illite and chlorite which make up the bulk of the rock. The high concentrations of base cations, silica and bicarbonate in the groundwaters in comparison with atmospheric inputs and soil waters shows that weathering is the dominant source. The stream waters have about 3 to 4 times the concentration of Sr and higher $^{87}\text{Sr}/^{86}\text{Sr}$ in rainfall and therefore a major component of weathering-derived Sr must be present. The groundwaters have concentrations of Sr more than two orders of magnitude greater than that found in rainfall and soil water and therefore must be dominated by weathering derived Sr from the bedrock. It is not, however, possible to calculate weathering rates due to the lack of knowledge of residence time of the groundwaters.

The maximum Sr isotope ratio found in the groundwaters is similar to that extant during diagenesis when the system was homogenised through the smectite-illite transition. This implies that the weathering phase is Rb-poor or Rb-free because no further increase in $^{87}\text{Sr}/^{86}\text{Sr}$ has occurred since the Ordovician/Silurian. The groundwaters and surface waters initially show a positive correlation with Si, Na and Ca implying that a phase containing these elements is the main control on the weathering of Sr. It is proposed that the controlling phase is a plagioclase feldspar which is present in the bedrock and which is likely to be the relatively easily weathered based on known stability relationships. It is often postulated that the dominant source of Ca in streamwaters (and by inference Sr) is from minor carbonate veins along bedrock fractures. In fact, high Ca in the Hore has been assumed to be due to calcite dissolution from an old Pb-Zn mine in the headwaters of this stream. This is indicated by relatively high Ca/Sr ratios in the Afon Hore streamwaters ($0.4 - 0.5 \times 10^3$ compared to typically $0.2 - 0.3 \times 10^3$ in the Hafren). The highest Ca concentrations were found in the Tanllwyth but here Ca/Sr ratios are similar to the Hafren and the Sr is likely to be from a non-carbonate source as indicated by the relatively high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the streams.

The importance of weathering in the groundwater environment is well established but it is not clear how much of this Sr is transferred to streams during baseflow or stormflow conditions. The very high Sr concentrations in the deeper groundwaters are much higher than the streamwaters, even at baseflow, and it is unlikely that they contribute directly to streamflow generation as discussed previously in section 6. Mixing between shallow and deeper groundwater from the deeper fractures may take place but if this was significant in terms of volume the deeper waters would quickly become diluted to lower Sr concentrations and variable Sr isotope ratios. The shallow groundwaters are considered to form an important component to streams as discussed in section 6. As a consequence the shallow groundwaters should also be considered in terms of the estimation of weathering rates.

It is clear that the weathering style of the soils and bedrock in the groundwater zone are different with different mineral assemblages dominating each. The groundwater environment is dominated by the weathering of feldspar (and possibly calcite), whereas soil weathering appears to be more intense and weathering of smectite minerals occurs. The acid soils at Plynlimon are generally base-poor and it is likely that groundwaters potentially provide an important contribution to generating alkalinity and neutralising acidity in these acid upland streams.

7.3 Weathering rates in the Plynlimon catchments

The fact that groundwater supplies base cations to streams implies that the weathering of large volumes of bedrock in the groundwater environment is important in terms of catchment output. Weathering rates calculated here are based on total output from streams and may not be truly representative of weathering rates within the catchment: any export of groundwater from the catchment means that calculations based on stream export are minima. In addition biomass uptake may also take up large amounts of base cations and further underestimate weathering rates, and changes in the cation exchange pool may have a significant positive or negative effect on the calculation of weathering rates. The uptake of base cations by biomass represents a large repository of base cation storage and small changes in the amount of biomass may lead to significant errors in mass balance measurements in catchments. Whether uptake of base cations occurs in the soil zone or directly from shallow groundwater is also critical to the effects of acidification of soils because proton release occurs through roots in response to cation uptake to keep charge balance. It is generally considered that long term flux measurements are necessary to average out the latter effects, because small term fluctuations will be averaged out if the system is at steady state. However, this is an assumption, and although based on long term catchment studies over periods of decades, it cannot be fully deduced that the time periods are long enough to be certain of steady state conditions in aggrading/degrading forest systems or where long term changes due to acidification are occurring.

Robson & Neal (1996) have studied long term statistical variations in the Plynlimon catchments and concluded that long term trends are not apparent for most elements including base cations in the Plynlimon

catchments. A steady state system is, therefore, assumed. In addition, it is assumed that there is insignificant losses of base cations from the groundwater system of the catchments due to groundwater loss along the valley system.

Providing that the end member compositions are known and that they are of constant composition, mixing is generally a simple calculation if only two components are present. The isotopic composition of Sr in waters and the various cation pools represents a mixture of atmospherically derived and weathering derived Sr. However, the weathering component may be variable depending on a) the degree of weathering, and b) local mixing between the many potential physical sources within catchments. The isotopic composition of Sr in atmospheric deposition is similar to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater in coastal areas, whereas continental dust sources may be important in non coastal areas. The weathering component is primarily controlled by the relative solubility's of minerals in the catchment but which may be distributed in the soil exchange pool and within the biomass as well the bedrock. A knowledge of this source, transfer rates and mechanisms of Sr exported from catchments as well as the distribution of Sr within catchments is essential to an understanding of the catchment response to changing geochemical conditions. If weathering rates are low then cation depletion within the soil exchange pool in response to acidification may take place leading to acidification of stream waters and groundwater.

Strontium in the waters can be treated in the present study as representing a simple two component mixture of strontium from atmospheric inputs and strontium derived from weathering. The atmospheric input end member is taken to have a concentration of $2.1 \mu\text{g l}^{-1}$ (flow weighted mean of rainfall; Neal et al., 1992) and an isotopic ratio of 0.7092. The weathering end-member is more difficult to estimate. If we assume that the maximum isotope ratio found in the groundwaters represents the weathering value of the groundwater system, then 0.7149 is a reasonable estimate. Mixing based on this estimate assumes that the streamwaters represent mixing between groundwater and atmospheric inputs as concluded in the previous section. It is evident, however, that higher ratios are present as Sr bound to the soils in both the podzol and gley (Tables 5.4 and 5.5). The dominant soil, the podzol has porewaters with a similar Sr isotope ratio and the exchangeable ratio is only slightly higher than this (0.7162). Therefore, the weathering-derived strontium is considered to be justified at a ratio around these values.

The isotope ratios in runoff are intermediate between the precipitation and weathering derived Sr and it is therefore possible to calculate the fraction of Sr derived from each component. If we assume simple mixing between rainfall and rock weathering derived Sr, this indicates that between 60 % and 80 % of the Sr in the three streams is derived from weathering with the Tanllwyth containing the most and the Afon Hafren the least. The main Severn, Afon Hafren and Afon Hore show little variation with flow similar to variations noted in other studies (Wickman & Jacks, 1991; Bain & Bacon, 1994). The Tanllwyth (and to a lesser degree the other streams) shows a decrease in Sr isotope ratio at high flows indicating a larger atmospheric-derived component. The long term flow weighted concentrations and isotope ratios derived in this study can be used to calculate weathering rates for Sr (Wickman & Jacks, 1992):

$$W \% = \frac{\left[\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_R - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_D \right]}{\left[\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_W - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_D \right]} \times 100$$

where R, D and W refer to runoff, deposition and weathering respectively.

Strontium isotopes have been used as a surrogate to estimate the behaviour of Ca in many catchment

studies (Åberg et al., 1990). This is because the two elements show similar chemical behaviour in simple ecosystems (Wickman & Jacks, 1991). The application of Sr isotopes to the major cation Ca may, however, be complicated by different behaviour or to sources with different Sr/Ca ratios. Strontium tends to show a slightly greater affinity for adsorption sites on clay minerals (Nesbitt et al., 1980), but such differences are relatively small as both are extremely mobile during weathering in most weathering environments. The similar behaviour of Sr and Ca in the present study is indicated by the good correlation of these elements in the streams and groundwaters (Figure 7.2). Weathering rates for Ca have been calculated assuming similar behaviour for Sr and Ca:

$$\text{Weathering rate} = D_{Ca} \times \frac{W \%}{(100 - W \%)}$$

Long term flux measurements for the Hafren and Hore have been calculated using Sr isotopes and are shown on Table 7.1 along with calculations based on mass balance (Durand et al., 1994).

Stream	Estimate based on $^{87}\text{Sr}/^{86}\text{Sr}$		Estimate based on mass balance	
	Sr	Ca	Sr	Ca
Afon Hafren	57	8.5	51	10.6
Afon Hore	74	16.3	52.1	18.4

Table 7.1 Weathering rates for the Afon Hafren and Afon Hore catchments based on $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (flow weighted) and mass balance calculation (Durand et al., 1994). Weathering-derived $^{87}\text{Sr}/^{86}\text{Sr}$ assumed to be 0.7149 and Sr and Ca fluxes based on long term stream output. Sr in $\text{g ha}^{-1} \text{yr}^{-1}$ and Ca in $\text{kg ha}^{-1} \text{yr}^{-1}$.

The budgets calculated by Durand et al. (1994) were considered to be an "indicator of the biogeochemical functioning of the catchments, rather than as an exact balance of the elements". This was suggested because of the problems with estimating solute fluxes in streams due to the lack of continuous monitoring of geochemical compositions which tends to bias calculations to low flow concentrations. The estimates for Sr and Ca weathering rates based on Sr isotopes are also shown on Table 7.1. The rates for the Hafren are very similar to those obtained by mass balance, particularly for Sr. The calculations for the Hore, however, are similar for Ca but not for Sr, which has a much higher estimated weathering rate of Sr using the Sr isotope method. The measured long term flux of Sr for the Hore and Hafren are similar (101 and $104 \text{ g ha}^{-1} \text{ year}^{-1}$) but the isotope ratio in the Hore stream is significantly higher.

There are several potential reasons why the weathering rate of Sr does not match more precisely the mass balance calculations. Firstly the stream output ("weathering") is truly biased toward baseflow and although Sr is higher in baseflow, the fluxes are much greater during stormflow. This would lead to higher stream flux because of higher Sr concentration measured in baseflow and therefore greater loss from the catchment. Secondly, it is possible that the Sr concentration and flux in atmospheric input is too high. This may be due for example to the poor precision at the very low concentrations present in rainfall, but the calculation appears to agree for the Hafren. Thirdly, one of the end-member ratios chosen in the isotope mixing technique is not correct. This is most likely to be the weathering end member e.g. if the ratio of 0.7048 chosen from the groundwaters is not representative of the total weathering-derived Sr in runoff. The soils were collected from the Hafren catchment and it may be the case that weathering in the Hore soils is different e.g. more intense.

8. CONCLUSIONS

Strontium isotopes have been used as a natural tracer to determine the dominant flowpaths of water through the Plynlimon catchments and to indicate weathering rates and processes. The isotope ratios in soil porewaters and on exchange sites are very variable and the porewaters are not in equilibrium with strontium on the exchangeable sites, most likely as a result of rapid transit times and discrete transport pathways. The large variation in isotope ratios is due to mixing between weathering- and atmospherically-derived sources.

The strontium in streamwaters also represents a mixture of strontium from atmospheric and weathering sources. Although there is a regional variation in isotope ratios in waters from different parts of the catchment, the local variations are small over large amounts of stream discharge. This implies that the streams are largely derived from a well-mixed source. The streamwaters lie on a mixing line between most of the groundwaters and rainfall implying that these form the dominant inputs even at high flow. Shallow groundwaters are similar chemically and isotopically to the streams and it is concluded that flow routing and mixing through the shallow bedrock fracture system is important in streamflow generation. The fact that there is such a small and consistent variation implies that the waters do not represent recent mixing as this would produce significant scatter depending on the antecedent conditions and amount of rainfall. This is consistent with stable isotope studies, which imply that the stream water is dominated by pre-event older water.

Weathering rates have been calculated assuming a two component mixing between atmospherically-derived and weathering-derived strontium and these generally show good agreement with previously published mass balance studies. Weathering varies considerably in the soils with intensive weathering in the B horizon podzols where sheet silicates are being weathered. This is thought to be relatively small quantitatively in comparison with deeper mineral soils where the dominant active weathering occurs. Relatively long residence time waters are present at depth and weathering is thought to be dominated by the weathering of plagioclase feldspar. Dissolution of calcite occurs in the upper parts of the Afon Hore catchment but the isotope signatures imply that there is not a significant effect on strontium concentrations and isotope ratios. The shallow groundwaters, present in shallow fractured bedrock, form a zone of mixing between rainfall and the deeper groundwaters although the volumes of deeper groundwater contributed are small and mainly isolated from the shallow system.

The conclusion of this study that flow routing through shallow bedrock fractures is important and that a well mixed groundwater provides much of the stream input even at high flow, are important factors to be considered in terms of water quality models and resource management in upland catchment systems.

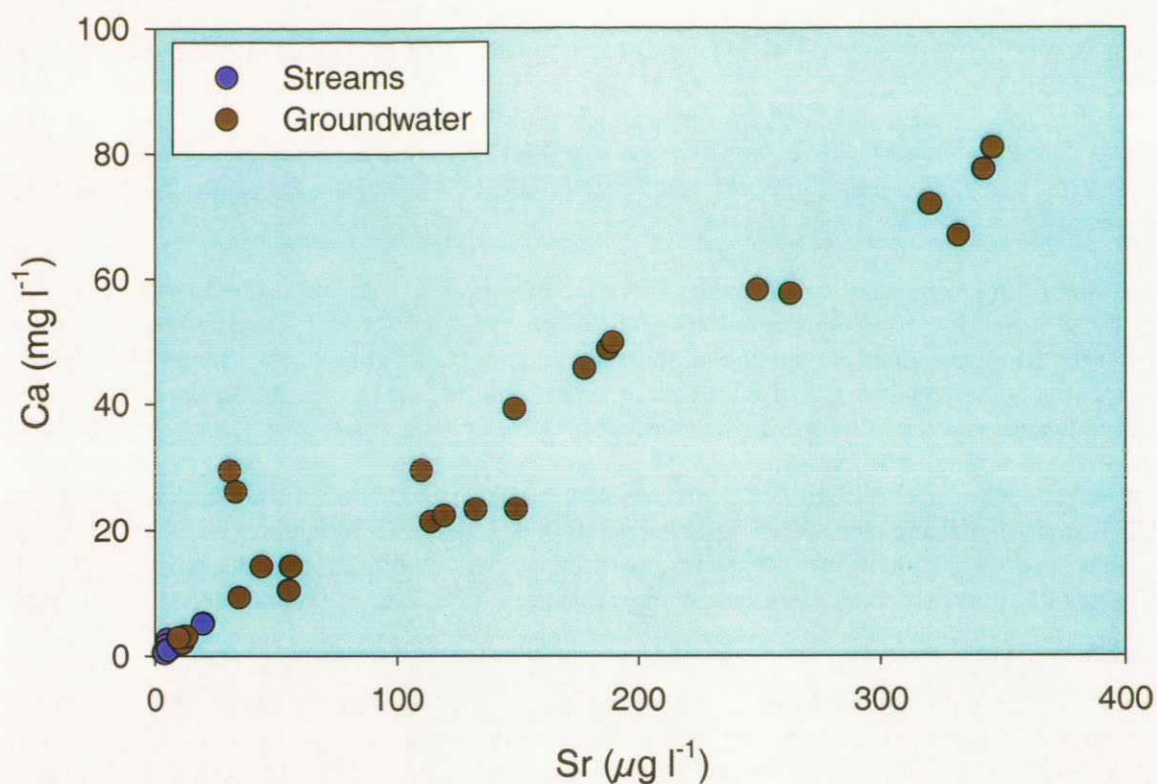


Figure 7.2 Plot of Sr vs. Ca in the Plynlimon streams and groundwaters.

Higher Ca concentrations in the Hore catchment have previously been taken as evidence of calcite dissolution from an old Pb-Zn mine in the Upper Hore and the higher weathering rate in the Hore may be due to calcite dissolution, the kinetics of which are much faster than silicate dissolution. Calcite dissolution, however, would lead to lower $^{87}\text{Sr}/^{86}\text{Sr}$ in the Hore catchment, the opposite to what is actually measured in the Hore stream. It is difficult to say at present which if any of the above is likely to be correct. Nevertheless, it appears that Sr isotopes provide a means of estimating weathering rates, and certainly for the Afon Hafren stream, the rate is comparable to mass balance techniques but more simple to calculate because it does not necessitate an accurate knowledge of input fluxes.

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