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Geological Survey**
NATURAL ENVIRONMENT RESEARCH COUNCIL



**Environment
Agency**

Baseline Report Series: 17. The Ordovician and Silurian meta- sedimentary aquifers of central and south-west Wales

Groundwater Systems and Water Quality
Commissioned Report CR/05/034N

Science Group: Air, Land & Water
Technical Report NC/99/74/17



The Natural Quality of Groundwater in England and Wales
A joint programme of research by the British Geological Survey and
the Environment Agency

BRITISH GEOLOGICAL SURVEY
Commissioned Report CR/04/034N

ENVIRONMENT AGENCY
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Aberystwyth Grits on the shore at Aberystwyth.

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Baseline Report Series: 17. The Ordovician and Silurian meta-sedimentary aquifers of central and south-west Wales

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FOREWORD

Groundwater issuing from springs has been regarded since the earliest recorded history as something pure, even sacred. In its natural state, it is generally of excellent quality and an essential natural resource. However, the natural quality of groundwater in our aquifers is continually being modified by the influence of man. This occurs due to groundwater abstraction and the consequent change in groundwater flow, artificial recharge and direct inputs of anthropogenic substances. A thorough knowledge of the quantity and quality of groundwaters in our aquifers, including a good understanding of the physical and chemical processes that control these, is therefore essential for effective management of this valuable resource.

About 35 per cent of public water supply in England and Wales is provided by groundwater resources, this figure being higher in the south and east of England where the figure exceeds 70 per cent. Groundwater is also extremely important for private water supplies and in some areas, often those with the highest concentration of private abstractions, alternative supplies are generally not available. Groundwater flows and seepages are also vital for maintaining summer flows in rivers, streams and wetland habitats, some of which rely solely on groundwater, especially in eastern and southern England. The quantity and quality of groundwater is therefore extremely important to sustain both water supply and sensitive ecosystems.

Until now there has not been a common approach, either in the UK or across Europe, to define the natural “baseline” quality of groundwater. Such a standard is needed as the scientific basis for defining natural variations in groundwater quality and whether or not anthropogenic pollution is taking place. It is not uncommon for existing limits for drinking water quality to be breached by entirely natural processes. This means that it is essential to understand the natural quality of groundwater to enable the necessary protection, management and restoration measures for groundwater to be adopted.

One of the main problems pertinent to groundwater remediation issues concerns the background or baseline to which remedial measures must, or can, be taken. Naturally high concentrations of some elements in particular areas may make it impossible or uneconomic to remediate to levels below the natural background which may already breach certain environmental standards. The Baseline Reports Series assesses the controls on water quality which are responsible for causing the natural variations seen in groundwater and provides a background for assessing the likely outcomes and timescales for restoration.

This report builds on a scoping study of England and Wales, carried out in 1996 by the British Geological Survey for the Environment Agency, which reviewed the approach to be adopted in producing a series of reports on the principal aquifers in England and Wales. The initial phase of this work was completed in 1998 and comprised reports on seven aquifers. This report forms part of the second phase of the work that will extend coverage to all the important aquifers in England and Wales. The Baseline reports will be of use not only to regulatory agencies but also to all users of groundwater, including water companies, industry and agriculture, and all those involved in the protection and remediation of groundwater.

BACKGROUND TO THE BASELINE PROJECT

The baseline concentration of a substance in groundwater may be defined in several different ways. For the purpose of the project, the definition is given as

“the range in concentration (within a specified system) of a given element, species or chemical substance present in solution which is derived from natural geological, biological, or atmospheric sources”

Terms such as background or threshold can have a similar meaning and have often been used to identify “anomalous” concentrations relative to typical values e.g. in mineral exploration. There may be additional definitions required for regulation purposes, for example when changes from the present day conditions of groundwater may represent the starting point of monitoring. This may be defined as background and such an initial condition may include some anthropogenic component in the water quality.

In order to interpret the water quality variations in terms of the baseline, some knowledge of the residence times of groundwater is required. For this purpose both inert and reactive chemical and isotopic tracers are essential. Measurement of the absolute age of groundwater presents many difficulties and radiocarbon dating is the most widely used technique. By investigating the evolution of water quality along flow lines it may be possible to establish relative timescales using a combination of geochemical and isotopic methods. Indicators such as the stable isotope composition of water may also provide indirect evidence of residence time. The identification (or absence) of marker species related to activities of the industrial era, such as total organic carbon (TOC), tritium (^3H), dissolved greenhouse gases -chlorofluorocarbons (CFCs) - and certain micro-organic pollutants may provide evidence of a recent component in the groundwater. The baseline has been modified by man since earliest times due to settlement and agricultural practices. However, for practical purposes, it is convenient to be able to distinguish water of different 'ages': (i) palaeowater - recharge originating during or before the last glacial era i.e. older than c.10 ka (ii) pre-industrial water (pre 1800s), (iii) water predating modern agricultural practices (pre 1940s) and (iv) modern post-nuclear testing era (post 1963).

Thus an ideal starting point is to locate waters where there are no traces of human impact, essentially those from the pre-industrial era, although this is not always easy for several reasons. Groundwater exploitation by means of drilling may penetrate water of different ages and/or quality with increasing depth as a result of the stratification that invariably develops. This stratification is a result of different flow paths and flow rates being established as a consequence of prevailing hydraulic gradients and the natural variation in the aquifer's physical and geochemical properties. The drilling and installation of boreholes may penetrate this stratified groundwater and pumped samples will therefore often represent mixtures of the stratified system. In dual porosity aquifers, such as the Chalk, the water contained in the fractures may be considerably different chemically from the water contained in the matrix because of differences in residence time. The determination of the natural baseline can be achieved by several means including the study of pristine (unaffected by anthropogenic influence) environments, the use of historical records and the application of graphical procedures such as probability plots to discriminate different populations (Shand & Frengstad, 2001; Edmunds et al., 2003). The “baseline” refers to a *specified system* (e.g. aquifer, groundwater body or formation) and is represented by a range of concentrations within that system. This range can then be specified by the median and lower and upper limits of concentration.

The BASELINE objectives are:

1. to establish criteria for defining the baseline concentrations of a wide range of substances that occur naturally in groundwater, as well as their chemical controls, based on sound geochemical principles, as a basis for defining water quality status and standards in England and Wales (in the context of UK and Europe); also to assess anomalies due to geological conditions and to formulate a quantitative basis for the definition of groundwater pollution.
2. to characterise a series of reference aquifers across England and Wales that can be used to illustrate the ranges in natural groundwater quality. The baseline conditions will be investigated as far as possible by cross-sections along the hydraulic gradient, in well characterised aquifers. Sequential changes in water-rock interaction (redox, dissolution-precipitation, surface reactions) as well as mixing, will be investigated. These results will then be extrapolated to the region surrounding each reference area. Lithofacies and mineralogical controls will also be taken into account. A wide range of inorganic constituents as well as organic carbon will be analysed to a common standard within the project. Although the focus will be on pristine groundwaters, the interface zone between unpolluted and polluted groundwaters will be investigated; this is because, even in polluted systems, the main constituents of the water are also controlled by geological factors, amount of recharge and natural climate variation.
3. to establish long term trends in water quality at representative localities in the selected reference aquifers and to interpret these in relation to past changes due to natural geochemical as well as hydrogeological responses or anthropogenic effects.
4. to provide a scientific foundation to underpin UK and EU water quality guideline policy, notably the Water Framework Directive, with an emphasis on the protection and sustainable development of high quality groundwater.

1. EXECUTIVE SUMMARY

The Ordovician and Silurian meta-sedimentary rocks of west and south-west Wales were originally deposited in the Welsh Basin, a deep marine basin bounded to the east and south by the Welsh Borders and South Wales. At this time, the basin was situated at the margin of the Iapetus Ocean, on the north-western edge of Gondwana in the southern hemisphere. The landscape of the region varies from steep sided valleys in the uplands to more gentle valleys filled with superficial alluvial and glacial deposits formed during the last glaciation.

This report presents data from groundwaters in south-west (Teifi Valley) and central (Rheidol Valley, upper Wye and Severn Valleys) Wales. These represent areas with different landscape characteristics: from steep headwater areas to flat valley bottoms; different land use, including managed coniferous forest, moorland and pasture; and contrasting geological environments comprising bedrock and Quaternary glacial deposits. The region is dominantly rural with many small towns and villages. Farming, forestry, light industry and tourism are an important part of the economy. Central Wales also has a legacy of former mining activities (Pb-Zn-Ag) which have impacted on the quality of surface waters.

The groundwater chemistry varies from very dilute in shallow groundwaters to moderately mineralised in deeper waters. Many groundwaters are slightly acidic due to a lack of reactive mineral phases in the bedrock, which is dominated by illite, chlorite and quartz. The younger groundwaters are typically of Na-Cl-SO₄ type, reflecting the importance of marine-derived atmospheric inputs, trending towards Ca-HCO₃ type in the older waters. The baseline chemistry is largely controlled by silicate dissolution reactions with additional sulphate from the oxidation of pyrite, a common accessory mineral in many of the shales and mudstones. The presence of carbonate minerals in superficial Drift deposits in part of the Teifi catchment has modified the baseline chemistry of the underlying bedrock groundwaters.

The fractured nature of the bedrock and the high transmissivity of sands and gravels in the superficial deposits make them susceptible to pollution. The occurrence of several sources with high nitrate, phosphorus, potassium and ammonium indicates that these waters are contaminated. However, for the majority of groundwaters sampled, the solute concentrations generally reflect the baseline.

2. PERSPECTIVE

Ordovician and Silurian mudstones, shales and grits occur over large parts of south-west and central Wales. These rocks have been weakly metamorphosed and typically form upland areas (including the Cambrian Mountains) with relatively steep valleys (Figure 2.1). The area is, in general, sparsely populated with many small towns and villages and a dominantly rural economy based principally on hill farming (Figure 2.2) and forestry. Larger towns, particularly on the coast (e.g. Aberystwyth, Cardigan), are important tourist centres. The area receives relatively high rainfall and is reliant to a large degree on surface water resources.

Three areas (Figure 2.3) have been selected where existing data allows a reasonable assessment of groundwater chemistry: i) the headwaters of the Severn and Wye near Plynlimon, central Wales; ii) the Teifi Valley in south-west Wales between Cardigan and Lampeter; iii) the Rheidol Valley east of Aberystwyth in central Wales. In these predominantly rural regions, groundwater in the bedrock and superficial deposits forms an important local resource, especially where mains water is not available.

The Ordovician and Silurian rocks of Wales have traditionally been considered to have low potential as a groundwater resource (Bassett, 1969). However, recent studies have shown that groundwater present in mudstones and shales (Neal et al., 1997a; Shand et al., 1999a; Haria & Shand, 2004), as well as in overlying Quaternary deposits (Hiscock & Paci, 2000; Robins et al., 2000) may form an important local resource as well as an important contributor to streams and rivers. The hydraulic relationship between bedrock and overlying superficial aquifers is poorly understood, and it has been suggested that many boreholes draw on storage from superficial aquifers, with abstraction through bedrock cracks and joints (Robins et al., 2000).

In the Teifi Valley, mains water in the catchment is provided by Dwr Cymru (Welsh Water), derived mainly from local surface water reservoirs. These are augmented by groundwater from the Olwen borehole [NGR 25817 24959], north of Lampeter, and by licensed abstraction from the Afon Teifi at Llechryd. There are many small abstractions from springs and boreholes, providing water for domestic households and farms. Glaciolacustrine deposits have been worked in the past as brick clays, and for mixing with coal dust in the manufacture of inferior fuel (Waters et al., 1997). Sand and gravel deposits are widespread and form an important resource (Figure 2.4). The bedrock has been used as a source of building stone, roadstone and rock fill.

The Plynlimon catchments form the headwaters of the rivers Severn (Afon Hafren and Afon Hore) and Wye (Afon Gwy). The upper reaches of the Wye are mainly grassland, used for sheep grazing, whereas the Afon Hafren and Afon Hore are forested with coniferous plantation. The groundwaters in these areas are not abstracted as a resource.

In the Rheidol Valley, there are no surface water supplies, due to contamination from old Pb-Zn mines in the catchment (Hiscock & Paci, 2000). Public and private water supplies are derived from both bedrock and superficial deposits, with the superficial deposits considered to offer the best potential for future development (Hiscock & Paci, 2000). Dams, tunnels and reservoirs constructed between 1957-62 are used for electricity generation in the Rheidol Valley.

There is a lack of hydrogeological and hydrochemical data over much the area underlain by Ordovician and Silurian meta-sedimentary rocks in Wales. Two areas of Wales, where relatively good hydrochemical data exist, have been selected as case studies: the headwaters of the Wye and Severn rivers close to Plynlimon and the lower reaches of the Teifi Valley in south west Wales. This is complemented by new sampling from springs and boreholes in the Rheidol valley of central Wales.

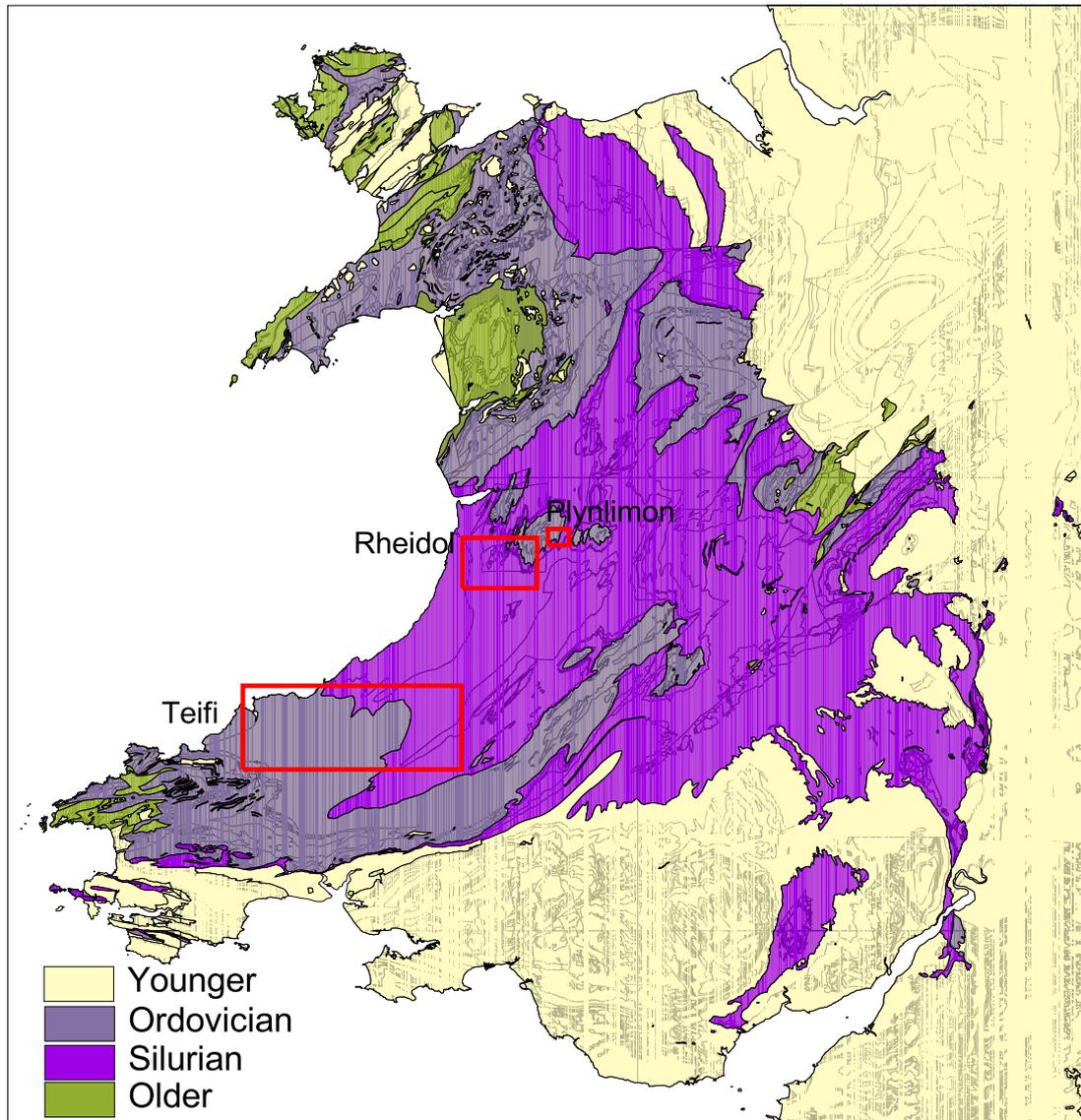
In the following report, the terms Severn Valley/catchment and Wye Valley/catchment refer only to those parts that were included in this study, namely the Afon Hafren and the Afon Hore in the Severn catchment and the Afon Gwy in the Wye catchment.



Figure 2.1 Rheidol Valley, central Wales showing typical scenery.



Figure 2.2 Upland farming forms an important part of the economy in much of central Wales.



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Figure 2.3 Simplified geology of Wales and the Marshes, highlighting the occurrence of Ordovician and Silurian rocks and the three areas selected for study.



Figure 2.4 Glaciofluvial sand and gravel pit, Penparc (from Walters et al, 1997).

3. BACKGROUND TO UNDERSTANDING BASELINE QUALITY

3.1 Introduction

An essential first step for assessing the natural (baseline) quality is an understanding of the geological and hydrogeological setting and the groundwater flow regime. To explain the characteristic groundwater chemistry, an understanding of the initial input(s) to the system (principally rainfall chemistry), together with knowledge of the mineralogy and geochemistry of the component minerals in the aquifer is also required.

3.2 Regional Geology

The Ordovician (510 to 439 Ma.) and Silurian (439 to 409 Ma.) periods were named after ancient tribes that inhabited North and South Wales. These Periods are subdivided into Epochs on the basis of graptolite (marine plankton fossils) biostratigraphy, shown on Table 3.1.

Table 3.1 Sub-divisions of the Ordovician and Silurian.

PERIOD	EPOCH	AGE AT BASE OF EPOCH (Ma)
Silurian	Pridoli	411
	Ludlow	424
	Wenlock	430
	Llandovery	439
Ordovician	Ashgill	443
	Caradoc	464
	Llandeilo	469
	Llanvirin	476
	Arenig	493
	Tremadoc	510

During the Ordovician and Silurian, a thick sequence of sediments were deposited in a sedimentary basin extending from the south-west to north-east across Wales to the Lake District. At this time Wales and England (part of Gondwana) lay south of the equator on the south-east margin of the Iapetus Ocean, whereas Scotland (part of Laurentia) lay close to the northern margin of the ocean. The Ordovician and Silurian sedimentary rocks of Wales and the Lake District were deposited in a marine environment, with sediment derived from the adjacent continent (Midland Platform) to the east and south.

Ordovician rocks in North Wales (around Snowdonia) comprise volcanic rocks (Tremadoc to Caradoc) up to several thousand metres thick, formed during subduction of the closing Iapetus Ocean, as well as sedimentary rocks. In South Wales, volcanic rocks are also present, but are mainly of Arenig to Llanvirin age. These are more abundant in South Wales near the coast, whereas inland, the rocks are mainly sedimentary mudstones and shales. The volcanic rocks at Builth and Llandrindod Wells are associated with major structural lineaments (the Pontesford-Linley lineament: an extension of the Towy Lineament). Sea-level fell towards the end of the Ordovician, but a major transgression of the sea from west to east occurred during early Silurian as a consequence of sea-level rise following climate warming and the ending of a major phase of glaciation. Uplift and erosion of the

adjacent landmass caused abundant sedimentation in the Welsh-Lake District areas. During this time the Welsh-Lake District Basin received mainly turbidite sediments with some early volcanism up to the Pridoli Epoch. In the west of Wales, the sediments are mainly deep water mudstones, shales and greywackes, but further east (Welsh Borders and Shropshire), in shallower environments, limestones, shales and shelly facies are present e.g. Wenlock Edge and around Dudley. The Llandoverly rocks of central Wales are mainly graptolitic shales and turbidites which reach a thickness of around 2500 m in the Plynlimon-Aberystwyth area. The end of the Silurian is marked by a change from marine to the terrestrial conditions of the “Old Red Sandstone”, which occurred during the Pridoli in Wales and the Welsh borders.

The sedimentary rocks underwent dewatering, uplift and folding as the Iapetus Ocean closed, ending with the Caledonian Orogeny in late Silurian-early Devonian times. The rocks were weakly metamorphosed during this time, but the grade of metamorphism is low, up to greenschist facies, and original sedimentary features are well preserved. The deformation is dominantly of a north-east “Caledonian” trend. The rocks are folded, with wavelengths being several km at a regional scale down to 50 m or less at the local scale. Faults also occur on a variety of scales, varying from major lineaments such as the Potesford-Linley fault and Church Stretton fault systems which separate the Welsh Basin from the Midlands Craton, down to the scale of metres.

The present day landscape was formed largely during the Tertiary and especially Quaternary times due to glaciation. The shallow bedrock is typically weathered, and present day shallow fracturing is likely to relate to Quaternary periglaciation and subsequent weathering controlled by the lithology and structural fabric of the rocks. It seems likely that much of the weathering profiles developed prior to the Quaternary were removed during glaciation.

3.3 The Plynlimon area

The Plynlimon catchments (Figures 2.3 and 3.1) are located approximately 20 km east of Aberystwyth. They form the headwaters of the rivers Severn (Afon Hafren and Afon Hore) and Wye (Afon Gwy). The hydrology of these catchments has been studied by the Centre for Ecology and Hydrology (formerly the Institute of Hydrology) for several decades (Kirby et al., 1991). The area of Wales between the Plynlimon catchments and Aberystwyth is mainly rural, with agriculture, forestry and tourism dominating the local economy. However, mining of Pb-Zn deposits was important in the late 19th and early 20th Centuries. The most important mines in the catchments of the upper Severn and Wye were the Nant Iago (Nant Iago is a tributary to the Wye) and the Snowbrook mine in the upper reaches of the Afon Hore. The groundwater data presented here are from sub-catchments with no previous history of mining.

Although groundwater in this region has traditionally been considered to be negligible, recent studies have identified the importance of shallow groundwater (Neal et al., 1997a) and its role in streamflow generation (Shand et al., 1997, 2001; Haria & Shand, 2004).

3.3.1 Geology of the Plynlimon area

The bedrock geology of the Severn and Wye headwater catchments comprises Ordovician and Silurian grits, mudstones and shales (Figure 3.2). However, the region has not been geologically mapped, except at a regional scale. The Ordovician rocks comprise the Fan Grits and Fan Shales of Ashgill and Caradoc age (Figure 3.2). The grits are tough, indurated rocks, but occur only locally along fault bounded margins in the upper reaches of the catchment. The dominant rock type in the upper parts of the catchments are the Fan shales, typically comprising soft grey mudstones and shales. The base of the Silurian rocks is represented by a hard mudstone horizon, the Rhaeder Mudstone (Breward, 1988). This forms a resistant band that causes cascades or small waterfalls where it is crossed by the streams (Figure 3.3). The overlying Gwestyn Shales are dark grey mudstones and

shales, in places containing abundant graptolite fossils and pyrite. The shales are typically weathered and fractured (Figure 3.4), occasionally with a yellow coloration due to oxidation of the pyrite and secondary precipitation of ferric oxy-hydroxides. The youngest rocks, the Frongogh Mudstones are mainly greenish-grey mudstones and are typically massive with well developed cleavage and found only in the lower reaches of the catchment.

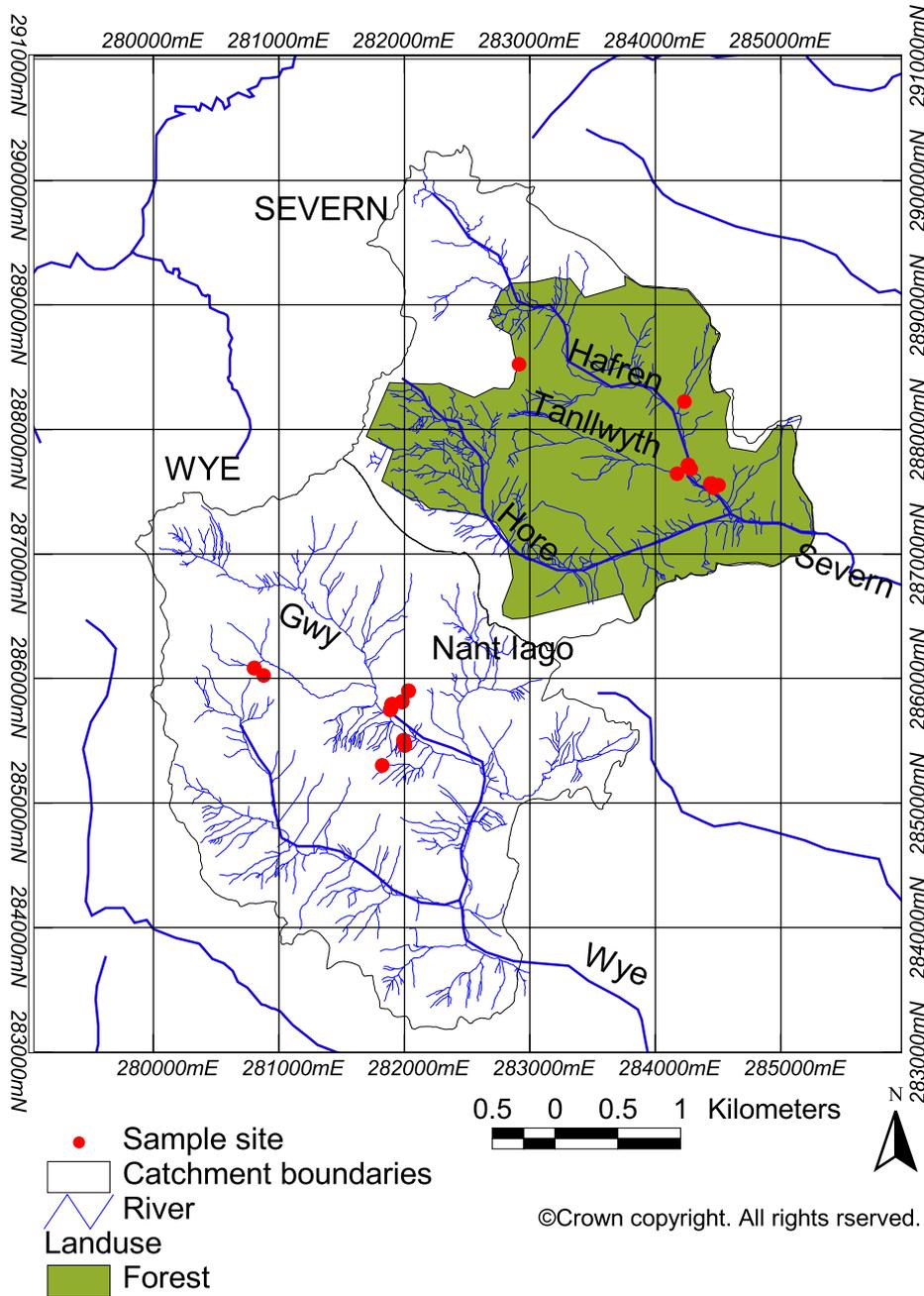


Figure 3.1 The Plynlimon catchments of the upper Severn and Wye Valleys. Landuse is displayed only for the marked catchment boundaries. The upper Wye and its tributaries are moorland and the upper Severn is largely forested. Sample sites used for study shown in text.

The bedrock was folded and faulted during closure of the Iapetus Ocean in late Silurian-early Devonian times. The main faults are associated with Pb-Zn-Ag vein mineralisation. The fault

controlling mineralisation in the Nant Iago (Figure 3.1) extends into the Severn catchment (Snowbrook Mine) in the upper reaches of the Afon Hore. The mineralisation is likely to be of Carboniferous age.

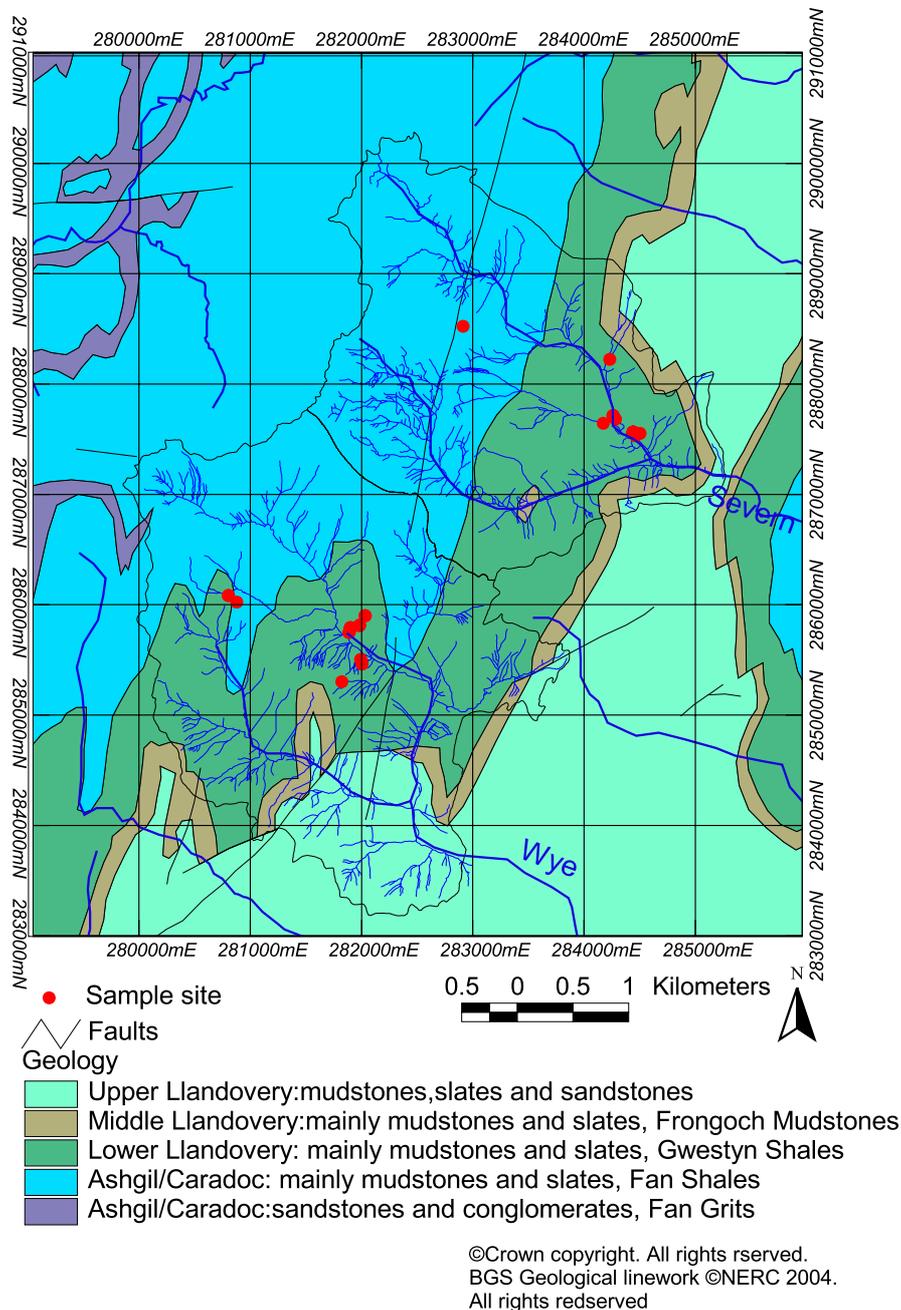


Figure 3.2 Geology of the Plynlimon catchments.

The forested Severn catchment contains limited Quaternary superficial deposits of glacial origin. A blue-grey clay was found during augering at the edge of the river at one site but its origin is not known. Alluvial deposits are locally present in the catchment, particularly at the confluence of the Afon Hafren and Tanllwyth. Augering in the Wye catchment showed a greater proportion of Quaternary deposits with till (boulder clay), slump and head deposits being common. More detailed understanding must await further study.



Figure 3.3 The Rhaeder Falls, in the forested Severn catchment cascades over the resistant Rhaeder Mudstone.



Figure 3.4 Fractured bedrock in the Gwestyn Shales, beneath thin podzol soils in the upper reaches of the Wye catchment.

3.3.2 Lithology and mineralogy

The mudstones are mainly composed of an iron magnesium chlorite, a dioctahedral mica (sericite/illite) and quartz, with lesser amounts of iron oxide. Weathering in the soils decreases with depth, with abundant vermiculite (from chlorite) being found in the upper soils. The Fan Grits are typically coarse feldspathic sandstones and grits, the feldspars being both plagioclase (albite-oligoclase) and orthoclase. Minor secondary calcite formed by deuteritic alteration of feldspar is also present, but uncommon. Pyrite is locally abundant in the Gwestyn Shales. The vein sulphide mineralisation in the former mines included argentiferous galena, pyrite and sphalerite with quartz and calcite as gangue minerals. Spoil heaps are found around the Nant Iago and Snowbrook mines.

3.3.3 Hydrogeology

The hydrogeology of the catchments has not been studied in detail. Boreholes were drilled in the Afon Hafren catchment in 1992 and 2000, and the Afon Gwy in 2002. Much of the work has focussed on hydrochemistry (Neal et al., 1997a; Shand et al., 1997, 1999a), but recent studies (Haria & Shand, 2004) aimed at assessing the importance of groundwater in streamflow generation, have monitored both hydrochemistry and physical measurements (water levels and soil potentials).

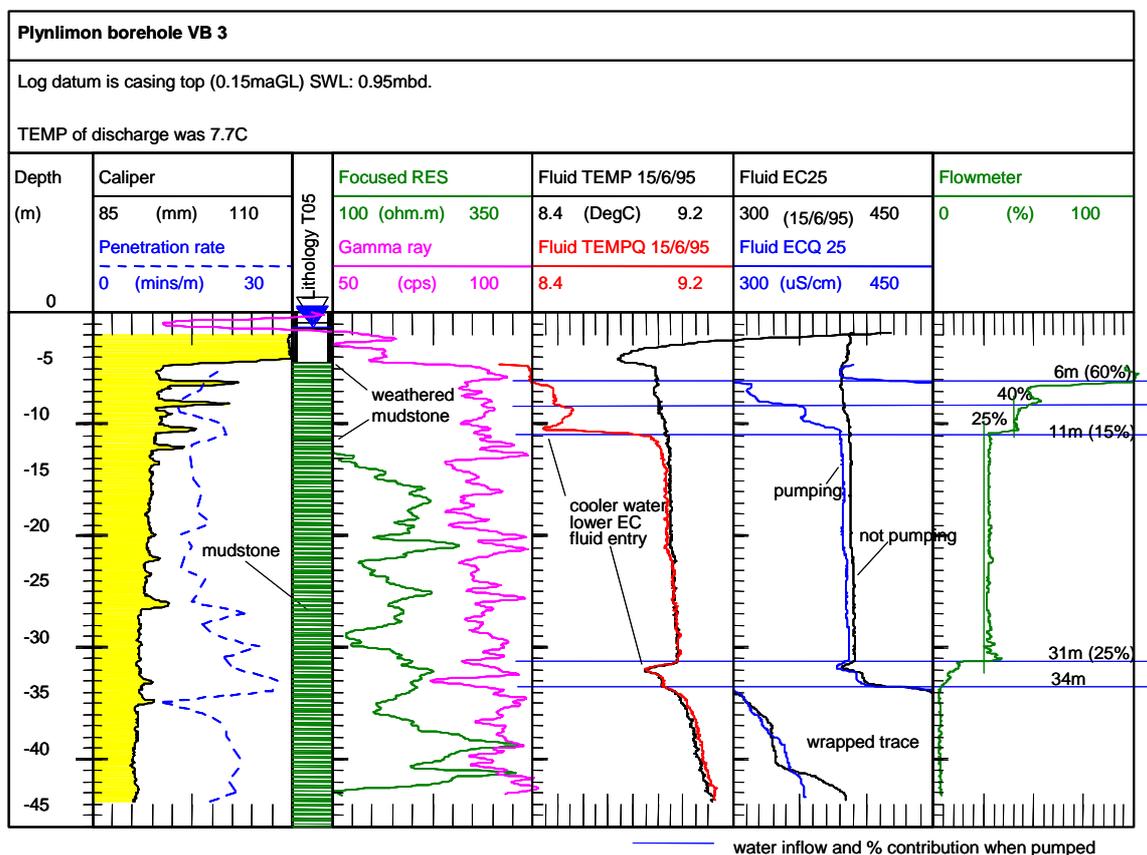


Figure 3.5 Geophysical log of a 50 m deep borehole in the Afon Hafren. The presence of fractures (horizontal blue lines) is indicated by the caliper log (left, yellow) and the temperature (red), SEC (blue) and flow meter readings (green) measured during pumping.

Geophysical logging techniques have confirmed evidence from outcrop exposures (Figure 3.4), that the bedrock is extensively fractured, particularly at shallow depth. Figure 3.5 shows a geophysical log from a 50 m borehole in the Afon Hafren catchment. Water from deeper isolated fractures had relatively high temperature and SEC (Specific Electric Conductivity), and these were interpreted as

being bedding plane fractures. The data also imply that in the shallow system (< 10 m), a series of hydraulically active fractures are present, indicated by flow logging and a stepped decrease in T ($^{\circ}$ C) and SEC. Some of the boreholes drilled were artesian, and some become artesian during rainfall events. Four boreholes from the lower slopes of the Afon Hafren provided specific capacities of 0.43, 0.48, 0.88 and $1.19 \text{ m}^3 \text{ hr}^{-1}$. An artesian borehole adjacent to the Tanllwyth stream had a much higher specific capacity of $14.4 \text{ m}^3 \text{ hr}^{-1}$ (D K Buckley, pers. comm. 2004). Water levels monitored monthly in boreholes from the upper slopes, intermediate slopes and valley bottom are shown in Figure 3.6. Water levels were close to the surface in the valley bottoms and showed little variation. The water levels were deeper below ground level in the upper slope boreholes, but these levels were much higher than on the slopes and valley bottom. Water levels are highest in the winter months when rainfall is highest. Due to the steep topography of the valleys, the main flow pathways are likely to be approximately orthogonal to the direction of the valleys. The degree of interconnectivity and fracture development determine the effective porosity of the rocks, but data are limited to estimate the spatial connection and the connectivity between deep and shallow fractures.

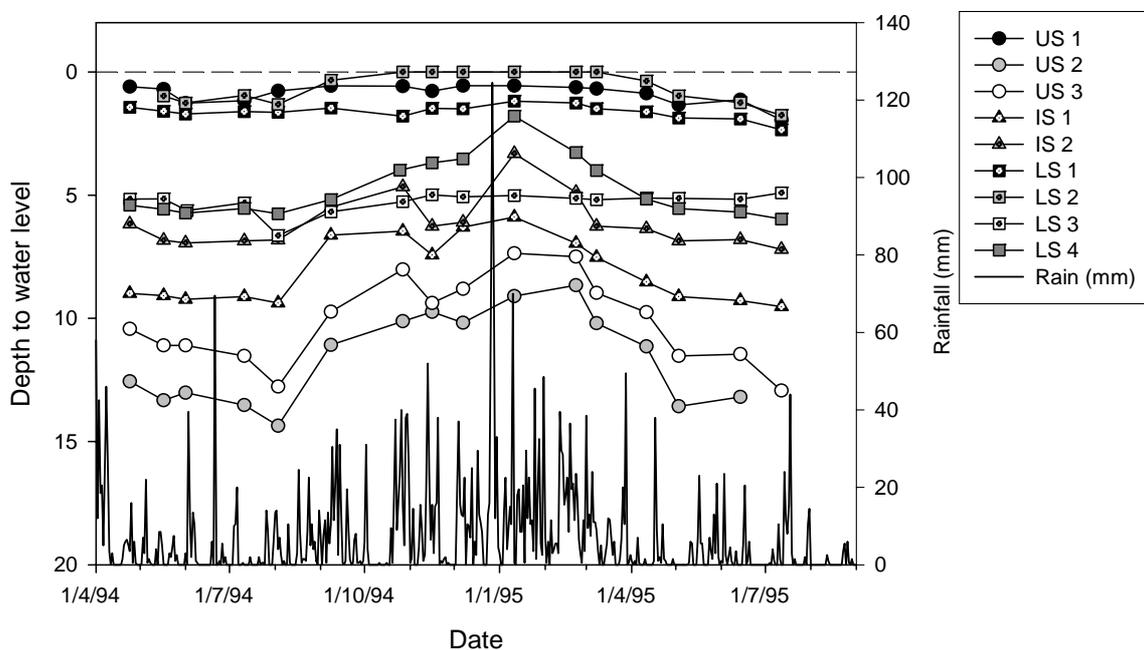


Figure 3.6 Water levels measured monthly in shallow boreholes for one year. Rainfall during the period is also plotted for comparison. The boreholes have been classed as upper slope (US), intermediate slope (IS) and lower slope (LS) based on their location in the catchment.

A detailed study site has recently been established in the catchment on the lower slopes and riparian zone of the Afon Hafren. Boreholes drilled to different depths and sealed using novel techniques (expanding polyurethane resin injections) were used to monitor head and chemical variations with time. Water levels in both shallow and deep fractures showed a similar, rapid response to rainfall (Figure 3.7) indicating rapid recharge to the bedrock (Haria & Shand, 2004). Discharge of groundwater into streams is considered to represent an important input to such upland streams, even during storm events, and may be an important control on stream water quality and ecosystem balance (Shand et al., 2004; Haria & Shand, 2004).

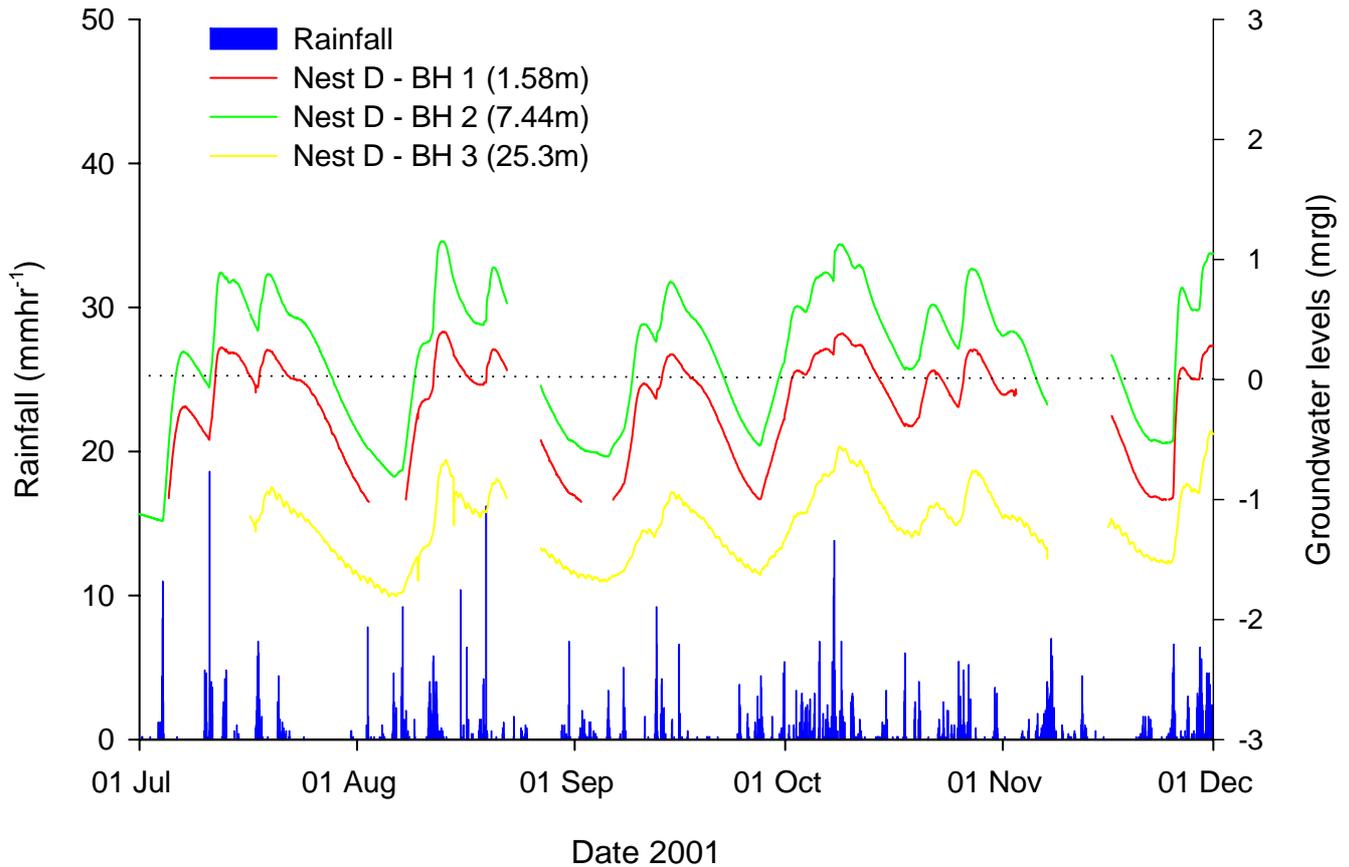


Figure 3.7 Water levels in piezometers situated close to the Hafren in the Severn catchment, showing higher heads in the deeper fractures.

3.3.4 Land use

The Afon Hafren and Afon Hore catchments are largely covered with coniferous plantation (Figure 3.1), dominantly Norway Spruce, Sitka Spruce, Lodgepole Pine, Scots Pine and Japanese Larch. The areas above the forest is mainly heather moor with some acid grassland. Felling and replanting have been undertaken during the past decade in different parts of the catchments. The Afon Gwy, in contrast is dominated by acid grassland (*Nardus* and *Festuca*) used for sheep grazing. The soils are generally thin (0.5-1m) and vary from peat on the upper plateau areas, podzols on the free draining slopes and peat and gleyed mineral soils in the valley bottoms.

3.4 The Teifi Valley

The Teifi Valley is dominantly rural, with agriculture and tourism dominating the local economy. The main towns in the study region (Figure 3.8) are Cardigan, and Lampeter in the west and east respectively with smaller towns between these including Newcastle Emlyn, Llandysul and Llanybydder.

3.4.1 Geology of the Teifi Valley

The bedrock of the Teifi Valley comprises a thick (> 5 km) sequence of Ordovician and Silurian (Figure 3.9) mudstones, with some siltstones and sandstones laid down between 450 and 420 Ma. The depth of water in which the sediments were laid was probably several hundred metres. Many form parallel-sided beds with sharp bases. Individual beds often show a fining upwards sequence and they are interpreted as having formed from fast moving, short-lived turbidity currents which carried

sediment from the edges of the basin across the basin floor. Thin beds of black, laminated pyritic mudstone or grey mottled mudstone occur between these “turbidite” units, and represent mud brought into the basins which settled slowly onto the ocean floor. These rocks were subsequently folding, faulted and uplifted during the Caledonian Orogeny in Late Silurian/Early Devonian times (Figure 3.10).

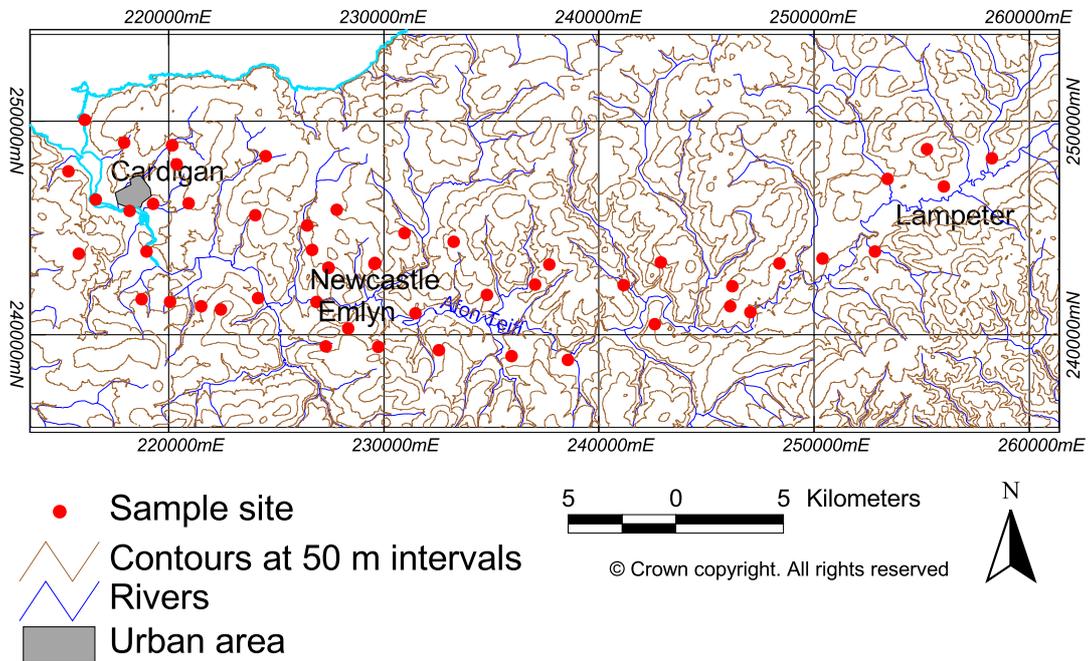


Figure 3.8 The Teifi Valley in south-west Wales showing topography and sample sites used in study.

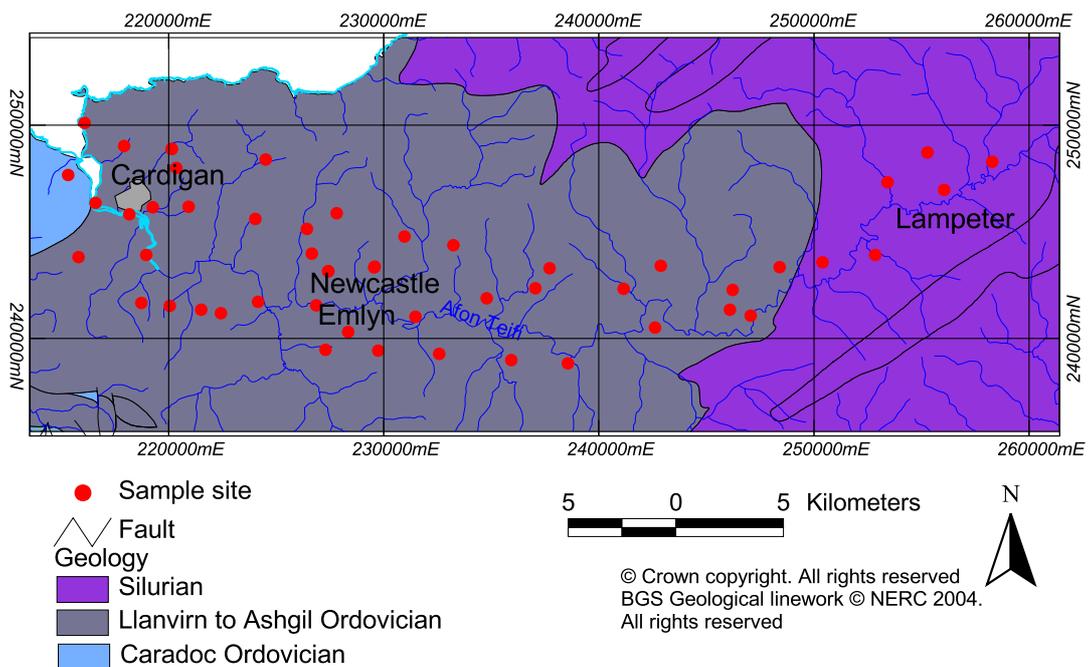


Figure 3.9 Simplified geology of the Teifi catchment.

The Ordovician and Silurian rocks in the study area (Waters et al., 1997) are dominated by mudstone, with variable proportions of sandstone and the succession is shown in Figure 3.11. The Molygrove Group consists of alternating mudstones, commonly rich in pyrite, and sandstones with subordinate pebble and mud-flake conglomerates. Rocks of the Nantmel Mudstones Formation cover much of the western part of the catchment. The rocks are mainly well cleaved silty mudstones, but in the west of the area, abundant units of sandstones are present. The Yr Allt Formation comprises dark grey, very silty mudstones, often showing slumped bedding, and the Cwmere Formation typically forms thinly interbedded laminated, dark-grey, pyritic mudstones. The main part of the Claerwen Group consists of thinly bedded, pale grey to green mudstones with diffuse siltstone laminae with fine grained sandstones increasing eastwards.



Figure 3.10 **Folded and faulted mudstones of the Molygrove Group (from Waters et al., 1997).**

The rocks of the catchment are complexly folded. The trends of the fold axes change from north-east – south-west in the east, to east-north-east – west-south-west at the coast. The wavelengths are several km at a regional scale to 50 m or less at the local scale. Faults also occur on a variety of scales. The mudstones and sandstones are locally well jointed and joint directions appear highly variable (Waters et al., 1997). A regional Caledonian cleavage is also evident in the mudstones of the Teifi Valley.

The bedrock in the area is partly covered by poorly consolidated drift (superficial) deposits (Figure 3.12). These comprise Quaternary glacial deposits including till (boulder clay), glaciofluvial sand and gravel and glaciolacustrine clays and silts as well as periglacial and post-glacial deposits such as head, peat, alluvium, alluvial fan deposits, river terrace deposits and tidal river deposits (Waters et al., 1997). The drift deposits may be up to 70 m deep in buried valleys. The main landscape features of the region formed during the late Tertiary and Quaternary times. Man-made deposits occur locally over both bedrock and drift deposits.

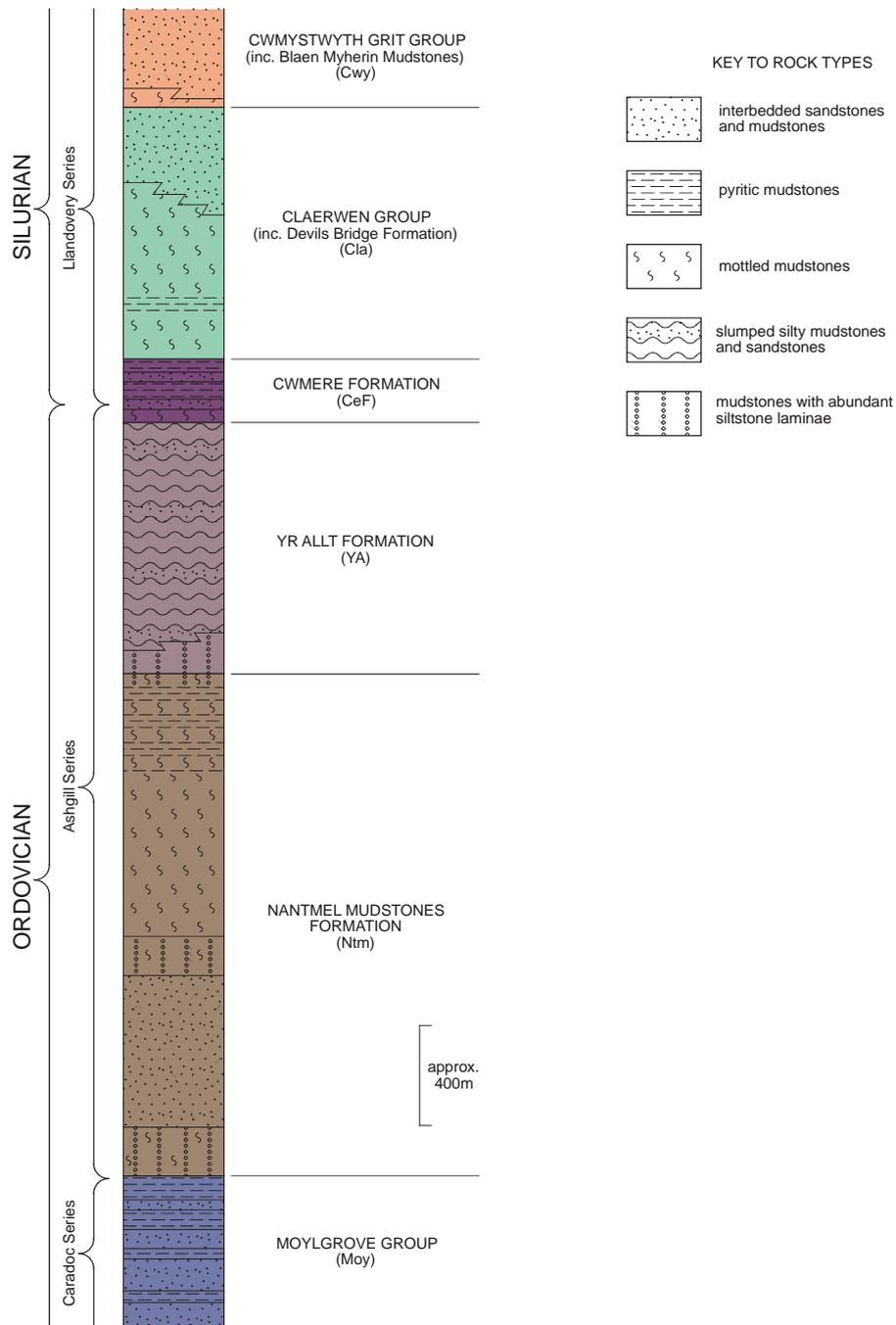


Figure 3.11 Stratigraphical succession of the Ordovician and Silurian rocks of the Teifi Valley (from Waters et al., 1997).

The original Afon Teifi probably flowed from much further north around Plynlimon, but during the Quaternary, the upper parts of this proto-Teifi was captured by the Afon Rheidol and Afon Ystwyth (Waters et al., 1997). The Quaternary deposits of the area have shown that two separate ice masses were present: the Welsh Ice Sheet descended from the Cambrian Mountains, leaving behind deposits dominated by Ordovician and Silurian rocks, whilst the Irish Sea Ice Sheet, sourced from much further north, occupied much of Cardigan Bay and its coastal tract (Waters et al., 1997). Tills of Welsh ice derivation are restricted to east of Llandysul, and Irish Sea-derived till is restricted to areas west of Aber-banc (NGR 2354 2417). A large glacial lake, Lake Teifi, once occupied much of the lower parts of the catchment during the Quaternary. This lake is considered to have formed during the

Devensian (15000 yrs BP), as retreating Devensian Irish Sea ice blocked the valley and impounded the glacial meltwater. The history of glacial advance and retreat, including lake formation, was complex and the reader is referred to Waters et al. (1977) for more details.

As the ice sheets retreated, mounds and ridges developed in the valley bottom and along the valley sides creating a number of blockages, which ponded melt water. The Afon Teifi cut through many of these deposits and, in places, abandoned its previous course to flow over bedrock. These areas form the gorges that are present today at, for example, Cenarth and Llanybydder.

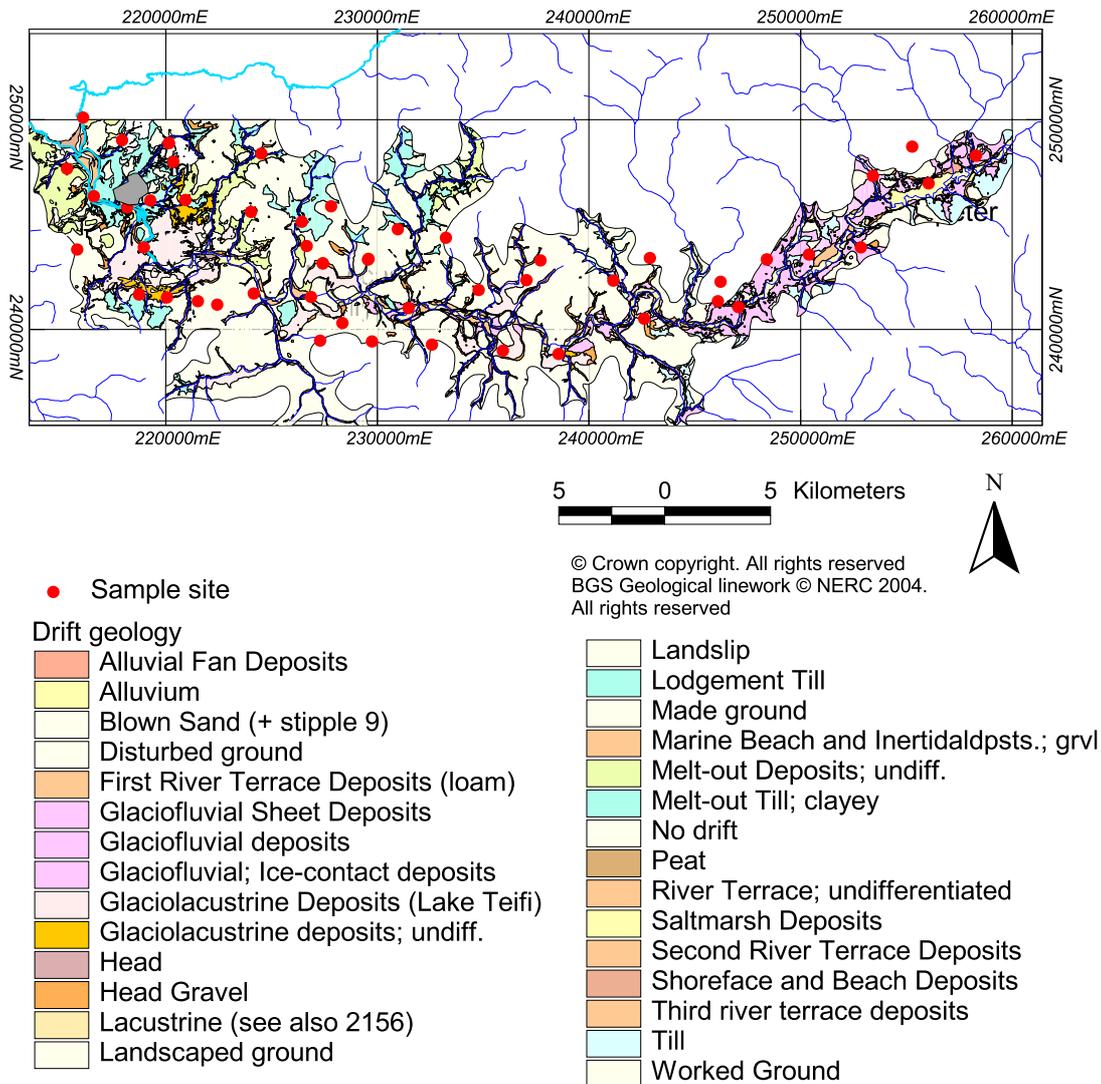


Figure 3.12 Superficial deposits in the valleys of the Teifi catchment. Areas in white are not mapped.

3.4.2 Lithology and mineralogy

The Ordovician and Silurian mudstones are dominated by illite and chlorite. Their mineralogy is similar to that found in the rocks of Plynlimon (section 3.3.2).

The mineralogy of the Drift deposits reflects their origin, with the eastern parts of the catchment being dominated by Lower Palaeozoic mudstones and sandstones. In the western part of the catchment, where Irish Sea Ice extended inland, the deposits contain, in addition, exotic rocks such as granites,

volcanic rocks, Carboniferous limestones, cherts and coal, Permo-Triassic sandstone, Cretaceous flint, Tertiary lignite and abundant Pleistocene marine shells. Small nodules of calcite are abundant in soil profiles developed on the Irish Sea Till, formed during dissolution and precipitation of shell material.

Alluvial gravels and sands often contain layers strongly cemented by manganese and iron oxides (hard pans). These may form barriers to flow and affect the chemistry by adsorption of trace metals. The lacustrine deposits of Lake Teifi are distinctive, blue-grey to chocolate brown clays. They are believed to be present under much of the modern alluvium of the Teifi Valley and underlie large areas of younger glacial deposits in the west of the study area, up to 70 m in thickness (Waters et al., 1997).

3.4.3 Hydrogeology

Two types of moderately permeable aquifer occur in the Teifi catchment: the solid bedrock aquifer and drift aquifers (Robins et al., 2000). The Lower Palaeozoic bedrock has traditionally been assumed to be impermeable due to the well cemented, indurated nature of the sediments. Their aquifer potential arises from the development of discontinuities in the rock mass, including bedding plane fractures, cleavage development, faulting and weathering. The highest transmissivities would be expected close to fault zones or in the shallower weathered bedrock.

The boreholes in the catchment are typically 35-50 m deep. These yield on average about $26 \text{ m}^3 \text{ d}^{-1}$. The average sustainable yield of a 40 m deep, 100 mm diameter borehole in the bedrock aquifer is 0.3 l s^{-1} (Robins et al., 2000). Water levels in the boreholes close to the valley bottom are generally shallow (0.5 – 2.5 m bgl) but increase on the valley sides, up to 12 m bgl. Single borehole pumping tests were carried out on three bedrock boreholes (Robins et al., 2000), yielding transmissivities between 0.3 and $1.1 \text{ m}^2 \text{ d}^{-1}$. It was concluded that boreholes in the catchment act as sumps for groundwater derived from superficial drift and weathered layers, as well as from deeper fractures (Robins et al., 2000).

The drift deposits of the catchment which provide the highest potential as aquifers are those which contain a high level of primary intergranular porosity, principally gravels and sands. However, many of these are heterogeneous and contain beds and lenses of clay making permeability variable in both a vertical and horizontal direction. In some areas, the permeable units may exceed 50 m in thickness, but major lateral differences in thickness are common (Waters et al., 1997). There are few abstractions directly from the drift, the public supply source from a 27 m borehole in sands gravels at Olwen (north of Lampeter, NGR 2582 2496) is licensed to abstract $395 \text{ m}^3 \text{ d}^{-1}$, and a constant rate pumping test indicated an aquifer transmissivity of $210 \text{ m}^2 \text{ d}^{-1}$ from early drawdown data (Robins et al., 2000). However, these may not be representative of many of the drift aquifers which are very heterogeneous. Yields of wells are similar to boreholes, and range up to $17 \text{ m}^3 \text{ d}^{-1}$.

There are numerous springs in the study area, which occur in three principal settings: i) solid bedrock; ii) at solid/drift contacts; iii) within drift (including many at permeable/impermeable drift contacts). The yields from the many springs are very variable, and many are classed as seepages. One source in head gravel and two in bedrock gave yields of between 170 and $260 \text{ m}^3 \text{ d}^{-1}$. Flows up to 5 l s^{-1} were recorded, with typical values being around 0.6 l s^{-1} (Waters et al., 1997).

There is little detailed information on the flow characteristics of groundwater and residence times in the aquifer. Estimated groundwater consumption in the study area is shown on Table 3.2. This is small compared with average flow in the Afon Teifi, indicating that groundwater sources could be developed further without impacting seriously on river flow. However, there is insufficient data to estimate the proportions abstracted from the drift and bedrock aquifers (Robins et al., 2000). It has been estimated, using the base flow index of the Teifi (0.54), that some 535 mm of the average runoff is derived from groundwater discharge. The fractured nature of the bedrock aquifer and the highly permeable sands and gravels of the drift aquifers make them vulnerable to contamination.

Table 3.2 Groundwater consumption ($\text{m}^3 \text{d}^{-1}$) in the Afon Teifi catchment (from Waters et al., 1977).

	Estimated use	Estimated number of abstractions	Total abstraction
Domestic – single property	0.6	809	485
Domestic > 25 people	1.2	83	100
Farm	1.5	68	102
Farm dairy	6.5	132	858
Commercial	8	20	160
Public supply	377		377
TOTAL		1113	2082

The hydraulic relationship between bedrock and the superficial aquifers is unclear. Groundwater in the bedrock is often locally confined and the superficial deposits contain argillaceous horizons which impede vertical flow and connectivity (Robins et al., 2000). Figure 3.12 shows a schematic section of the lower Afon Teifi Valley showing the potential flow pathways and interaction between the different water components of the catchment. Robins et al. (2000) concluded that the majority of the baseflow component (535 Ml a^{-1}) to the River Teifi derived from local recharge and lateral flow direct to the river. Longitudinal throughflow down the length of the (upper part) of the valley amounted to only about 490 Ml a^{-1} (Robins et al., 2000). Groundwater throughflow in the bedrock was estimated to be 9 Ml a^{-1} , modest by comparison.

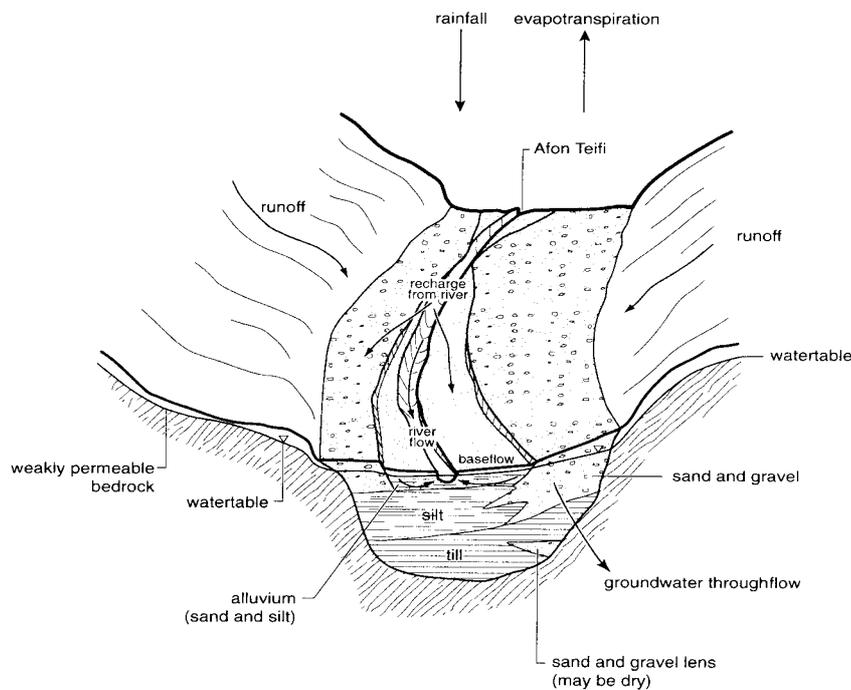


Figure 3.13 Schematic section of the lower Afon Teifi Valley showing the main flow components (after Robins et al., 2000).

3.4.4 Land use

The majority of the land use in the Teifi catchment is classed as managed grassland (Figure 3.14). Much of this is used for sheep farming. Managed forestry is also present, dominantly on the higher ground and small urban areas are located in many parts of the catchment.

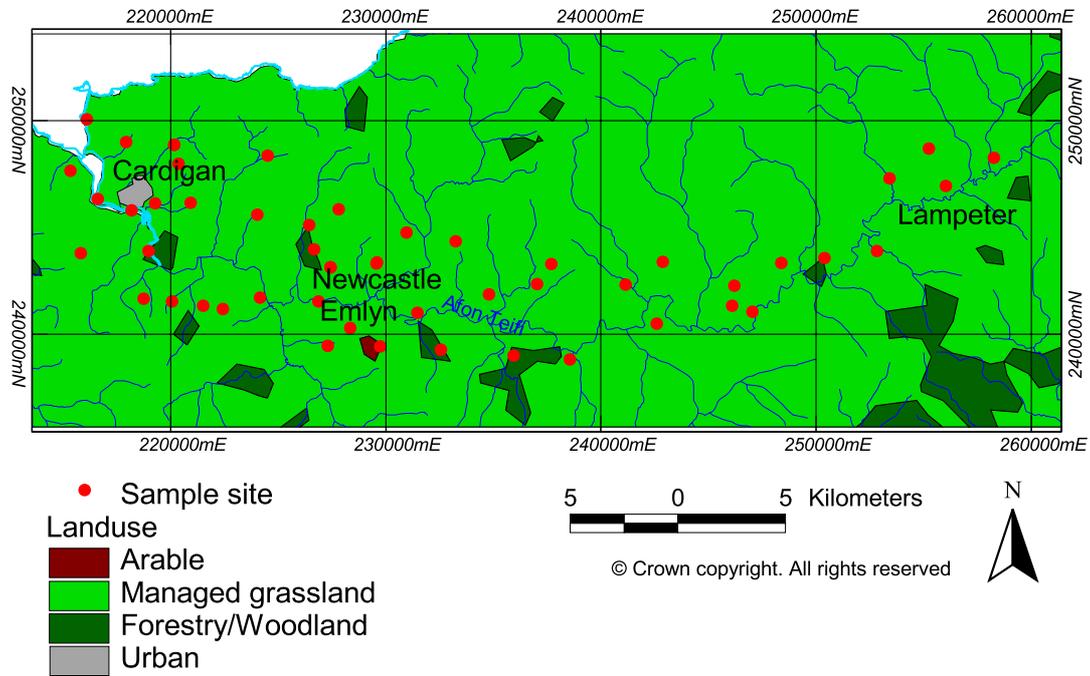


Figure 3.14 Land use map of the Teifi Valley.

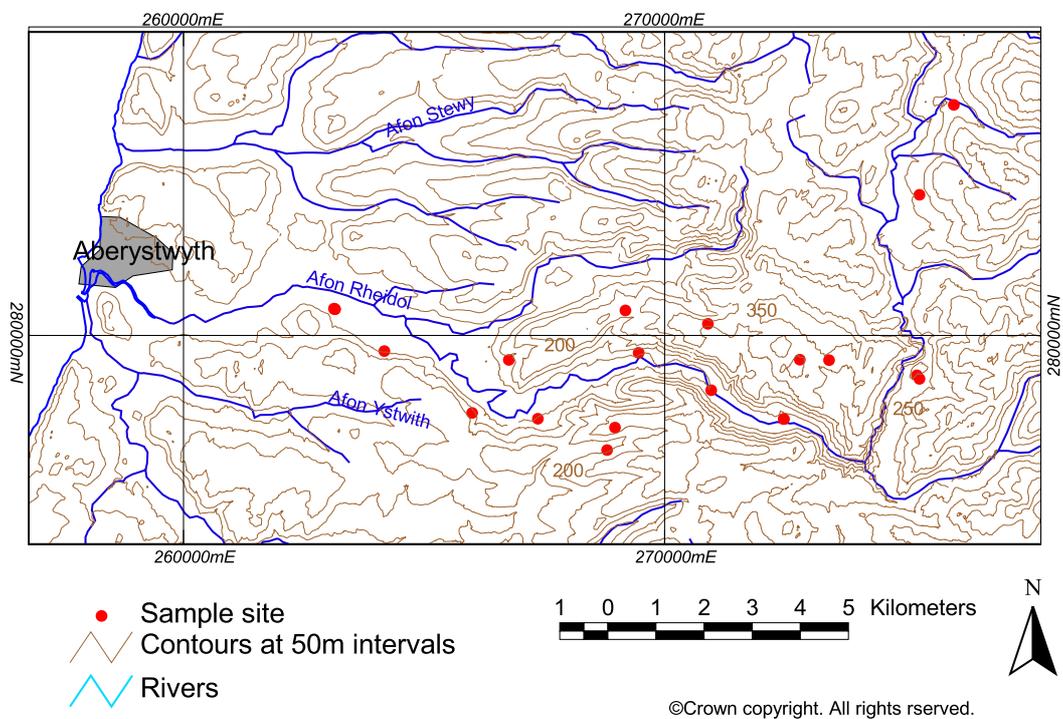


Figure 3.15 The Rheidol Valley in central Wales showing topography and sample sites used in study.

3.5 The Rheidol area

The Rheidol catchment study area (Figure 3.15) covers an area of approximately 180 km², rising from sea level at Aberystwyth to around 500 m at the source of the river Rheidol. The source of the River Rheidol is on the western flanks of Plynlimon. It initially flows southwards, but turns towards the west (near Devils Bridge) as a result of glacial capture, entering Cardigan Bay at Aberystwyth.

3.5.1 Geology

The bedrock of the catchment comprises Ordovician and Silurian mudstones, siltstones and sandstones, in places overlain by superficial Quaternary deposits (Cave & Haines, 1986). The stratigraphic sequence for the Ordovician and Silurian rocks is shown on Table 3.3 and Figure 3.16. The bedrock is mainly Silurian in age, but outliers of Ordovician age occur in the north-east near Plynlimon (Figure 3.17). The Llandovery rocks of central Wales are mainly graptolitic shales and turbidites which reach a thickness of around 2500 m in the Plynlimon area. The Ordovician rocks formed west of a submarine slope with deeper water to the west. Following a marine regression in the late Ordovician (related to a major glaciation), sedimentation resumed in the early Silurian (Llandovery) depositing a sequence of mainly mudstones and siltstones. During the early phase of sedimentation, influx of sediment was low and iron sulphide-bearing muds of high pelagic content accumulated (Cave & Hains, 1986). Sedimentation from the east or south-east continued with more turbiditic sediments which were coarser, producing alternating sand and mud. In the upper part of the Llandovery a change in the direction of sedimentation from south or south-west occurred, which produced the Aberystwyth Grits. The Aberystwyth Grits is composed dominantly of turbidites, formed from turbidity currents. Individual units comprise poorly sorted sandstones (greywackes) grading upwards into mudstones. Such cycles are often repeated giving an appearance of alternating sandstones and mudstones (see cover picture).

Table 3.3 Stratigraphy and lithology of the Silurian rocks in the Rheidol Valley.

AGE	SERIES	FORMATION	LITHOLOGY	THICKNESS (m)
Quaternary	Flandrian and Devensian		Peat, Head, Alluvium, Moraine, Till, River Terrace Deposits	< 30
Silurian	Llandovery	Aberystwyth Grits	Medium grey mudstone interbedded with pale grey medium to coarse grained sandstone	240
		Borth Mudstones	Medium to dark grey thickly bedded mudstone with thin beds of siltstone and sandstone	350
		Devil's Bridge	Grey thinly bedded mudstone, sandstone and siltstone	10-600
		Cwmsymlog	Grey mudstone with some siltstone and sandstone	0-140
		Derwenlas	Thinly bedded medium, pale grey mudstone with some siltstone and sandstone	20-80
		Cwmere	Dark grey thinly bedded pyritiferous mudstone with some thin siltstone beds	70-160

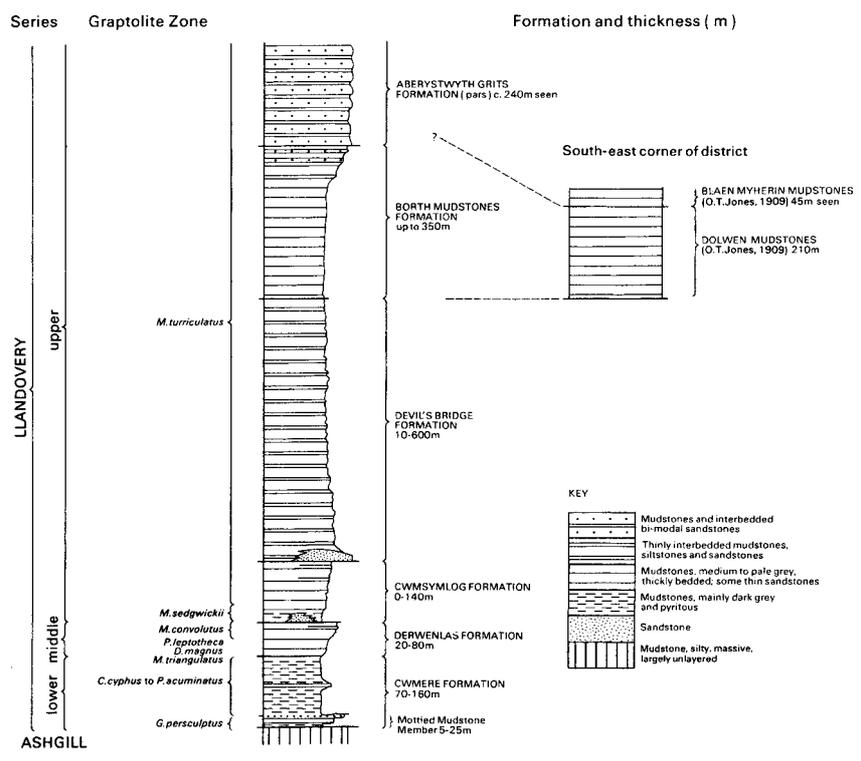
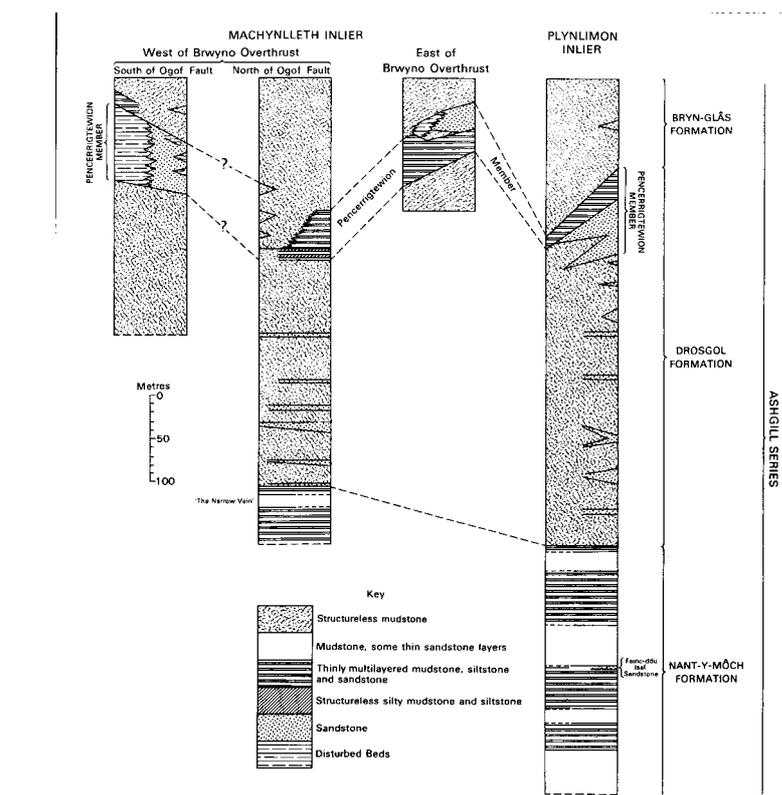


Figure 3.16 Stratigraphic sequence of Ordovician (top) and Silurian (bottom) rocks in the Rheidol Valley (from Cave & Haines, 1986).

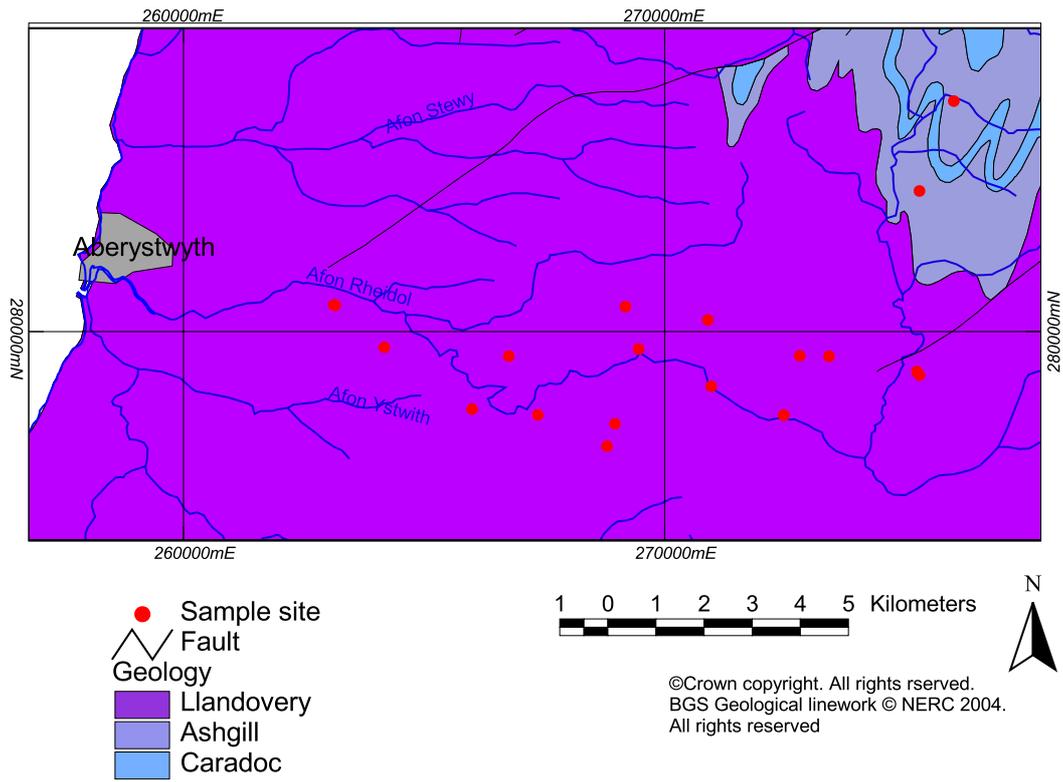


Figure 3.17 Simplified geology of the Rheidol Valley.



Figure 3.18 Vertical mudstones and slates of Llandovery age in the Rheidol Valley.

These sediments underwent weak metamorphism, uplift and deformation during the Caledonian Orogeny (Figure 3.18). The regional deformation formed a series of folds trending NNE with cleavage developed in a NNW-SSW direction sub-parallel to the folding. A single cleavage affects the rocks in the region, in general being spaced several millimetres apart. The major folds have wavelengths of about 10 km, but on the fold limbs, there are several orders of smaller folds (Cave & Hains, 1986).

The area is well known for the former mining of Pb-Zn mineralisation, particularly around Ystumtuen in the east of the valley. Acid mine drainage and drainage through spoil heaps has had a large impact on the surface waters, where pH can be as low as 2.6, and the stream waters may contain very high concentrations of heavy metals such as Pb, Zn Cd as well as Al (Fuge et al., 1991).

A complex series of Quaternary glacial and glaciofluvial deposits cover the bedrock, especially in the valley bottoms. There is no evidence for rocks being formed between the Silurian and the Quaternary. Ice masses originating from the higher ground around Plynlimon flowed outwards along the major valleys leaving behind a variety of deposits as the glaciers advanced and retreated (Figure 3.19). Glacial tills and moraines form heterogeneous deposits comprising mixtures of clays, silt, sand and gravel. The till deposits (boulder clay) are stiff blue-grey clays and silt with clasts of poorly sorted mudstone clasts. River terrace deposits are similar compositionally to the morainic drift, varying from poorly sorted sand, silt and clay to coarse sands and gravels. Much of the floodplain is covered with alluvial deposits. Head deposits are found on the slopes of the catchment especially in hollows, and comprise angular rock debris set in a matrix of silt and clay.

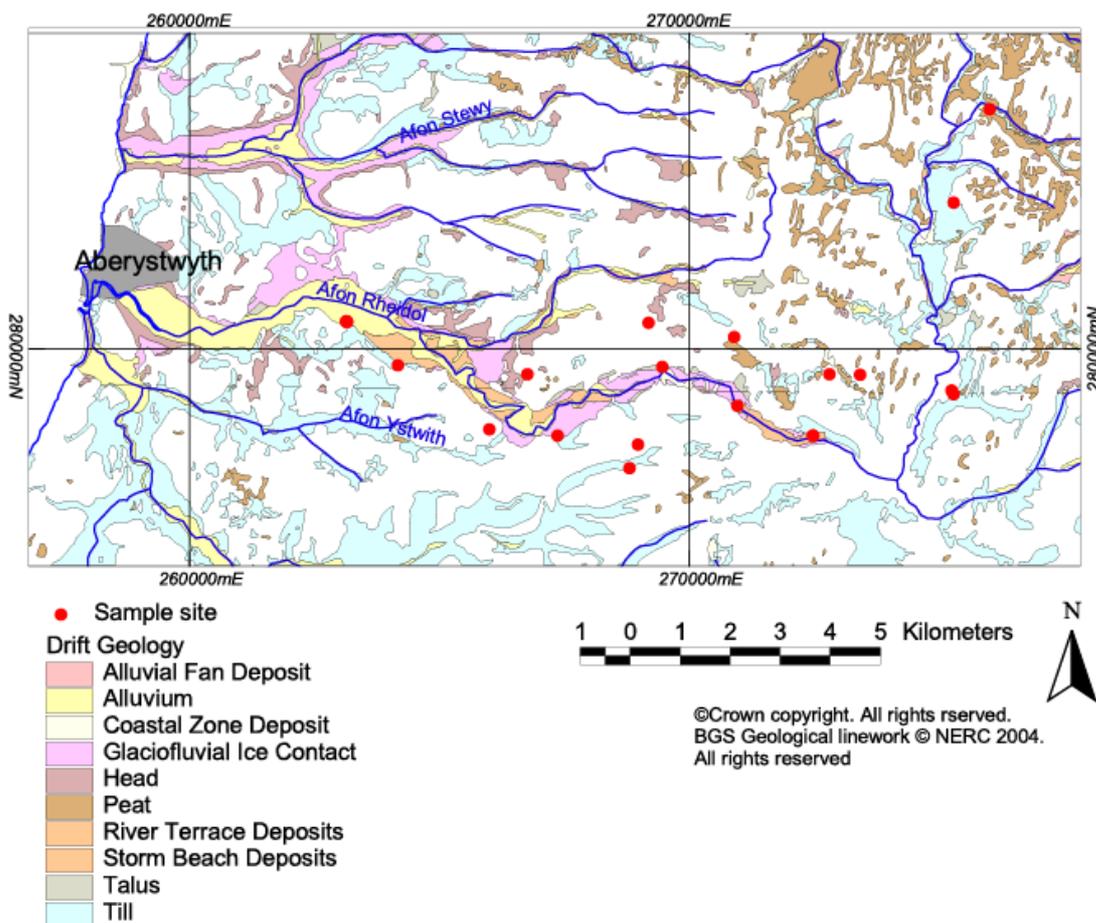


Figure 3.19 Geology map of the superficial deposits of the Rheidol Valley.

3.5.2 Hydrogeology

Hiscock & Paci (2000), using GIS applications, concluded that 25% of recorded abstractions fall on the boundaries between different geological units and, of these, two thirds relate to the contact between Quaternary deposits and bedrock. They concluded that the aquifer potential of the Silurian rocks is very limited. The metamorphic grade decreases upwards in the Silurian sequence and weathering increases, which, combined with the presence of thick bedded sandstones, increases groundwater potential. The permeability of the aquifer is controlled by the degree of fracturing and fracture connectivity which are heterogeneous at all scales. However, the degree of fracturing is greatest in the shallow part of the bedrock due to weathering. Many of the abandoned Pb-Zn mines were found to flood very rapidly, indicating that there is relatively good fracture connectivity in the bedrock (Hiscock & Paci, 2000). The near-surface weathered zone in the area is considered to be up to 20 m thick and the main bedrock groundwater potential is considered to be limited to the contact between the Aberystwyth Grits and Borth Mudstones Formations, or to the contacts between head deposits and bedrock (Hiscock & Paci, 2000). However, there are very few boreholes in the bedrock of this area and its groundwater potential remains untested.

Groundwater in the superficial Quaternary deposits can provide an important local resource e.g. boreholes (Lovesgrove, NGR 2638 2808) in the Rheidol Valley east of Aberystwyth sustain a yield of 3460 m³ d⁻¹ to public supply (Robins et al., 2000). The Quaternary deposits are mainly found on the lower hillslopes and valley bottoms (Figure 3.19), and are extremely variable and heterogeneous in terms of lithology. Till deposits forms a stiff clay unit which may act as a local confining layer. The valley alluvium is not considered a good aquifer as it contains layers of silt, clay and peat (Hiscock & Paci, 2000). The glaciofluvial deposits contain little silt and clay and form the best Quaternary aquifers. Transmissivities estimated from the Lovesgrove borehole are about 4000-6000 m² d⁻¹, specific yields about 5% and sustainable yield around 50 l s⁻¹ (Hyder Consulting Ltd., 1998). The thickness of these deposits is typically around 15-30 m. The River Terrace Deposits (Figure 3.19) also form relatively good aquifers with transmissivities of 500-1000 m² d⁻¹, storage coefficient about 2% and yield about 35-45 l s⁻¹ (Hiscock & Paci, 2000). Head deposits may form aquifers on valley sides and in hollows, but are of limited extent.

The relationships between bedrock and superficial deposit aquifers is poorly known. The fractured nature of the bedrock aquifer and the highly permeable sands and gravels of the drift aquifers make them vulnerable to contamination.

3.5.3 Lithology and mineralogy

The lithology of the Ordovician and Silurian sediments is very varied from mudstones to coarse sandstones. The more argillaceous sediments are typical of such rocks from elsewhere in the Welsh Basin being dominated by illite and sericite with some feldspar and these may also contain quartz, chert and rock pebbles. The coarser sediments e.g. in the Aberystwyth Formation, are quartz-rich (75 – 80%) sandstones, and are often feldspathic (commonly oligoclase-albite) with minor muscovite and carbonate minerals. Pyrite is a common mineral in some of the mudstones throughout the sequence. Phosphatic nodules and carbonaceous material have been reported in some of the Ordovician and Silurian mudstones. Ferruginous carbonate concretions have also been reported from the Borth Mudstones Formation (Denaeyer, 1948). Secondary Fe oxides are common, particularly on fracture surfaces where pyrite in the bedrock has been oxidised.

3.5.4 Land use

The dominant land use is mainly sheep with some dairy farming, classed as managed grassland (Figure 3.20). Approximately 30% of the catchment is forested (National Rivers Authority, 1996). The soils of the catchment are generally shallow, acidic and peaty (Hiscock & Paci, 2000).

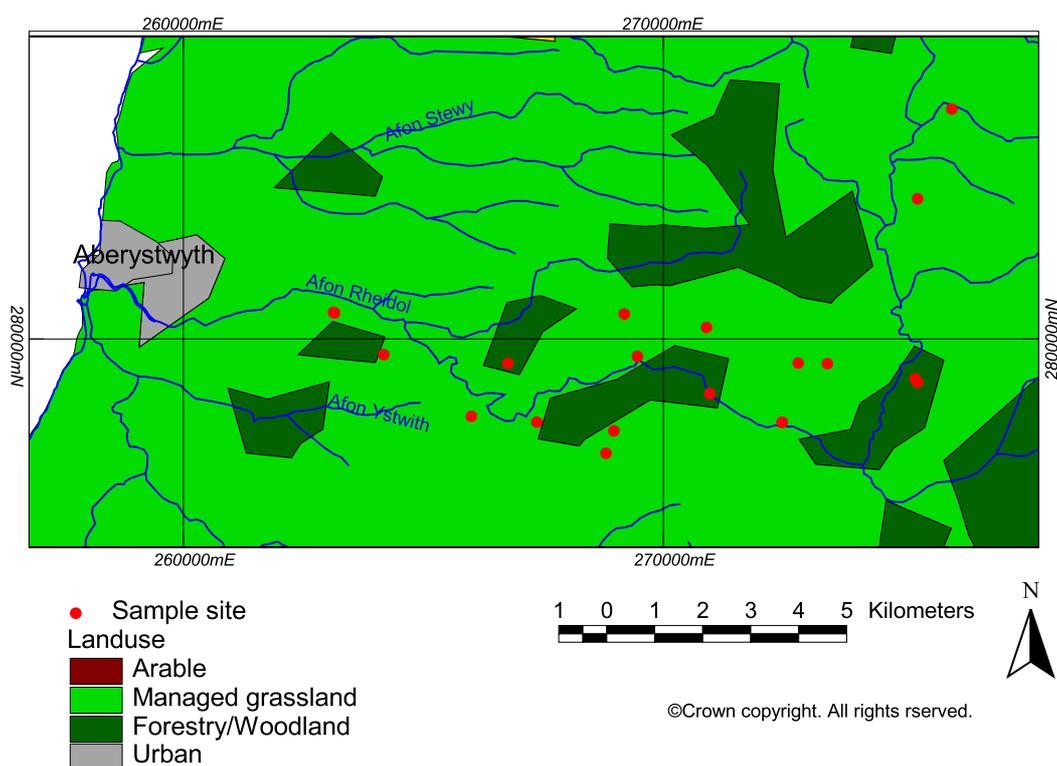


Figure 3.20 Land use map of the Rheidol Valley.

3.6 Rainfall chemistry

The rainfall in the Plynlimon catchments is relatively high with up to 2500 mm yr⁻¹ in the upper parts of the catchments. Nearly 40% of the rainfall falls in the months November to January (Brandt et al., 2004). The mean rainfall amount in the Rheidol catchment is 1790 mm (Hiscock & Paci, 2000). Average volume weighted rainfall chemistry is shown in Table 3.4 for the Plynlimon catchments for 1983 – 1995.

Table 3.4 Rainfall chemistry for the Plynlimon area in central Wales. The data in column 3 have been multiplied by 3 to allow for enrichment due to evapotranspiration. Data from Neal et al. (1997b).

Parameter	Concentration (mg l⁻¹)	Rainfall (x3)
pH	4.99	
Na (mg l⁻¹)	2.3	6.9
K (mg l⁻¹)	0.12	0.36
Ca (mg l⁻¹)	0.19	0.57
Mg (mg l⁻¹)	0.28	0.84
Cl (mg l⁻¹)	4.33	12.99
SO₄ (mg l⁻¹)	1.57	4.71
NO₃ (mg l⁻¹)	0.77	2.31
NH₄ (mg l⁻¹)	0.29	0.87
DOC	0.48	1.44
Ba (µg l⁻¹)	4.9	14.7
Br (µg l⁻¹)	16.4	49.2
Sr (µg l⁻¹)	2.0	6

4. DATA AND INTERPRETATION

There are limited hydrochemical data available for most of the outcrop area of Ordovician and Silurian rocks in Wales. Recent groundwater studies have been completed in two regions: the headwaters of the rivers Severn (Afon Hafren) and Wye (Afon Gwy), near Plynlimon in central Wales, and the Teifi Valley in south-west Wales.

4.1 Project sampling programme

The new sampling for this study focussed on the Rheidol Valley, east of Aberystwyth in central Wales. A total of 19 groundwater and two surface water samples were collected (Figure 3.15) during August 2004. The groundwater samples comprised 11 springs, 3 wells and 5 boreholes. In the majority of cases, it is not clear whether many of the springs and wells derived their water from bedrock, the superficial deposits or both. Of the borehole samples, one is derived from bedrock (Penrhiwlas, NGR 270894 280237) and four were collected from Environment Agency boreholes drilled into gravels in the Rheidol Valley at Ttering (NGR 263142 280544) and Ty Llwyd (NGR 267360 278248). Two river samples were also collected during the study as a comparison with the groundwater data: the Afon Rheidol at Rheidol Falls, NGR 270962 278844; and a stream adjacent to a sampled spring at Aberdwynant, NGR 272471 278241.

Where possible, the parameters pH, dissolved oxygen (DO) and redox potential (Eh) were measured on-site in an anaerobic flow-through cell (Figure 4.1). Other on-site measurements included temperature (T°C), specific electrical conductance (SEC) and alkalinity. Samples were collected for major and trace chemical analysis in polyethylene bottles. Those for major and trace elements were filtered through 0.45 µm filters and the aliquot for cation and trace elements was acidified to 1% v/v HNO₃ to minimise adsorption onto container walls. Major cations and sulphate were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP AES) and a wide range of trace elements by Inductively Coupled Plasma Mass Spectrometry (ICP MS). Nitrogen species were determined by colorimetry at the Environment Agency laboratories in Nottingham and the halogen (Cl, Br, I, F) elements analysed by automated colorimetry at the BGS laboratories.

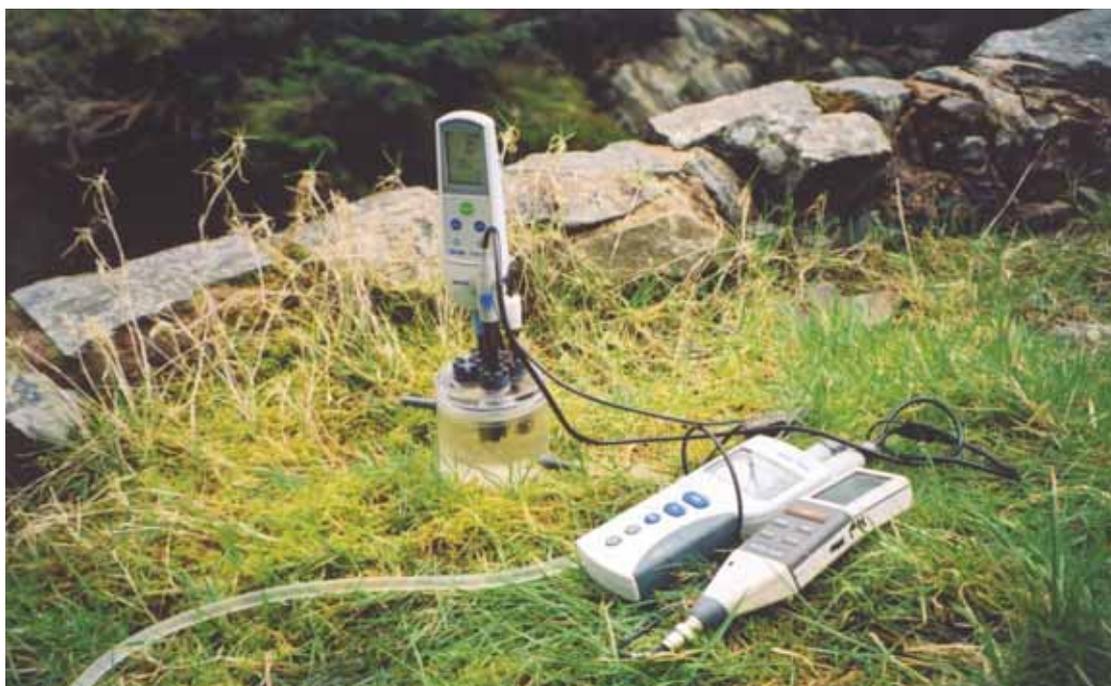


Figure 4.1 Measuring pH, Eh and DO in a flow-through cell.

Total and dissolved organic carbon (TOC and DOC) samples were also collected in Cr-acid washed glass bottles and, for the DOC samples, a 0.45µm silver-membrane filter was used. DOC was analysed by using a TOCSIN II analyser. Additional samples were also collected in glass bottles for stable isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$). Analyses were completed by mass spectrometry and the results reported relative to commonly used standard values, SMOW (Standard Mean Ocean Water) for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ and PDB (Pee Dee Belemnite) for $\delta^{13}\text{C}$.

4.2 Historical data

A total of 52 samples were collected in 1996 from the Teifi Valley between Cardigan and Lampeter (Figure 3.8). This included groundwater from 19 boreholes, 27 from springs and 6 from wells. Only 6 of these (5 springs and one borehole) are known to be derived wholly from superficial deposits. Two river samples were also collected from the river Teifi at Cenarth (NGR 226940 241580) during the sampling period.

Groundwater samples were collected from the headwater catchments of the Severn and Wye (Figure 3.1). The samples from the Severn catchment boreholes situated in the forested Afon Hafren catchment are from boreholes varying in depth from 1.5 to 50 m (22 boreholes). Many of the boreholes (1.5 – 30 m depth) have been sealed using permanent packers and the annulus sealed with expanding polyurethane foam, in order to stop mixing and bypass flow. The others, including the deepest boreholes (ca. 50 m), are open hole with approximately the top 5 m cased-off.

Samples were also collected from recently drilled boreholes in the Wye (Afon Gwy) catchment, all sealed to specific depths. These vary from 5 to 31 m depth.

4.3 Interpretation of pumped groundwater samples

The chemical composition of a groundwater sample will be a function of many factors. Variations in water quality may arise simply as a result of differences between the boreholes sampled, for example:

- differences in borehole design and construction
- different stratigraphic horizons being tapped
- different pumping histories

4.3.1 *Different borehole designs*

A groundwater sample from a specific depth in a fractured aquifer may represent a unique chemistry. However, boreholes penetrate different depths and may be open throughout much of their length allowing mixing to occur. Such problems have been noted in the Plynlimon catchment where samples from unscreened boreholes had an intermediate chemistry between those present in shallow and deep fractures (Figure 4.2). Differences in borehole design, in particular depth of borehole and depth of casing may therefore lead to the identification of differences in water quality not related to geochemical reactions along a simple 2-D flow path. In addition, the construction of a borehole is likely to disturb the original stratification of water quality and provide a pathway for water to migrate from zones of higher head to zones of lower head.

4.3.2 *Differences in stratigraphy*

Stratification of groundwater quality develops as a result of natural variations in the chemical and physical properties of aquifers. Pumped samples may represent a mixture of a stratified system. It is likely that differences in water chemistry will occur in different parts of the Ordovician-Silurian sedimentary sequence e.g. high SO_4 due to pyrite oxidation in the pyritiferous shales.

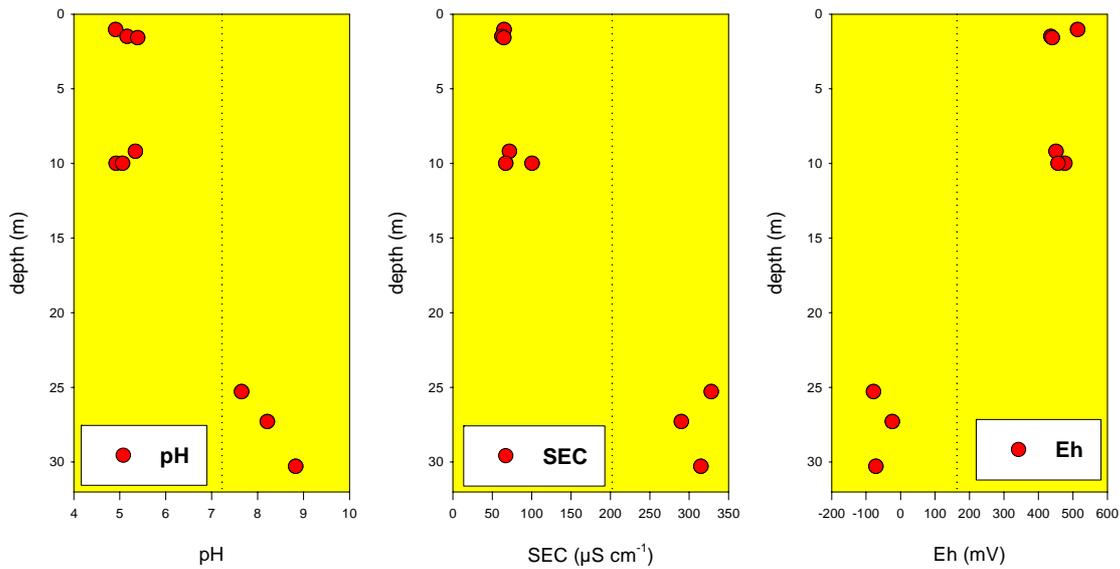


Figure 4.2 Depth variations of pH, SEC and Eh in piezometers from the Hafren (Severn) catchment. The dotted line shows the measured values in groundwater from an adjacent unscreened borehole.

4.3.3 Different pumping history

Groundwater abstraction, especially where large volumes of water have historically been pumped, is likely to have modified the groundwater chemistry from its original composition. For example, the pumping of fractures which have low transmissivity may result in younger, lower TDS water being drawn into these fractures. Extensive groundwater abstraction may also induce significant leakage from the overlying soils or permeable drift deposits which may influence the groundwater quality. Variable flow rates and differing hydraulic gradients within the aquifer may also exaggerate differences in groundwater chemistry.

This report presents a broad assessment of the water quality variations observed across the aquifer and the controlling geochemical processes. Chemical reactions are both time and space dependent and the data presented simply represents a snapshot of the water quality, which is in a constant state of change.

4.4 Data handling

For the purposes of this report, data with an ionic charge imbalance greater than 10% were rejected. Boreholes which were known to be contaminated or were situated in areas of point-source pollution were avoided. For plotting purposes, data below the detection limit were substituted with half of the detection limit. Changes in the detection limit, both with time and between laboratories often prove problematical in the calculation of average results.

5. HYDROCHEMICAL CHARACTERISTICS

5.1 Introduction

This section contains a summary of the hydrochemical characteristics of the groundwater in the study area. These are presented in summary tables for the different regions and, where known, the superficial groundwaters have been summarised separately. The tables show the ranges and averages of data as well as an upper concentration (mean + 2σ or 97.7th percentile) representing the upper limit of baseline in pristine waters. Where anthropogenic inputs are evident, an upper baseline has to be estimated (Chapter 8). The median is preferred to the mean as an average as it is more robust and less affected by extreme values. The 97.7 percentile is used as a practical cut off to define outlying data.

The summary data are shown graphically on a trilinear Piper Plot, boxplots and cumulative probability plots. The boxplots display the ranges of data and are designed to highlight the distribution of data on a percentile basis. The boxes show the range between the 25th and 75th percentiles, the whiskers represent the 10th and 90th percentiles and the dots the 5th and 95th percentiles. In addition, the median is shown as a horizontal black line and the mean as a blue line within the box. The solid black line on the boxplots represents a diluted seawater curve which has been normalised to the median Cl of the samples. This provides a general indication, in most aquifers, of inputs from water-rock interaction above the marine-derived (rainfall or connate) inputs. The solid grey line shows typical detection limits for each element.

Cumulative probability plots are useful in visualising the distribution of data and may be of use in determining outlying data or discerning pollution. Geochemical processes may alter the distribution of populations in several different ways giving rise to complex distributions. Box 5.1 illustrates how cumulative probability plots can be used to infer a range of processes occurring in the aquifer.

5.2 Plynlimon groundwaters

The summary data for the Plynlimon groundwaters is shown in Table 5.1 for major and minor solutes and Table 5.2 for trace elements. The groundwaters of the Severn and Wye have been sub-divided due to the contrasting land-use of the catchments, forested and moorland, respectively. The borehole depths vary from 1.5 m to 50 m.

5.2.1 *Water types and physicochemical characteristics*

Groundwater temperatures vary from 6 to 12 °C (Table 5.1), but these are typically 8-9 °C in the deeper boreholes. The range in pH is relatively large, from acidic in the shallow groundwaters to neutral or alkaline in some of the deeper boreholes. The SEC also varies from very fresh ($54 \mu\text{S cm}^{-1}$) to moderately mineralised ($328 \mu\text{S cm}^{-1}$). Redox conditions in the groundwaters tend to be more oxidising at shallow depths with high dissolved oxygen (DO) and Eh. This is more pronounced where the boreholes were sealed to specific depths, probably due to mixing in the borehole column of open boreholes (Figure 4.2).

Water types in both catchments are of similar type (Figure 5.1). The shallow groundwaters are typically Na-Cl-(SO₄) type and evolve in the deeper system towards Ca-HCO₃ type. Three samples from close to the riparian zone of the Afon Hafren are Na-HCO₃ type waters.

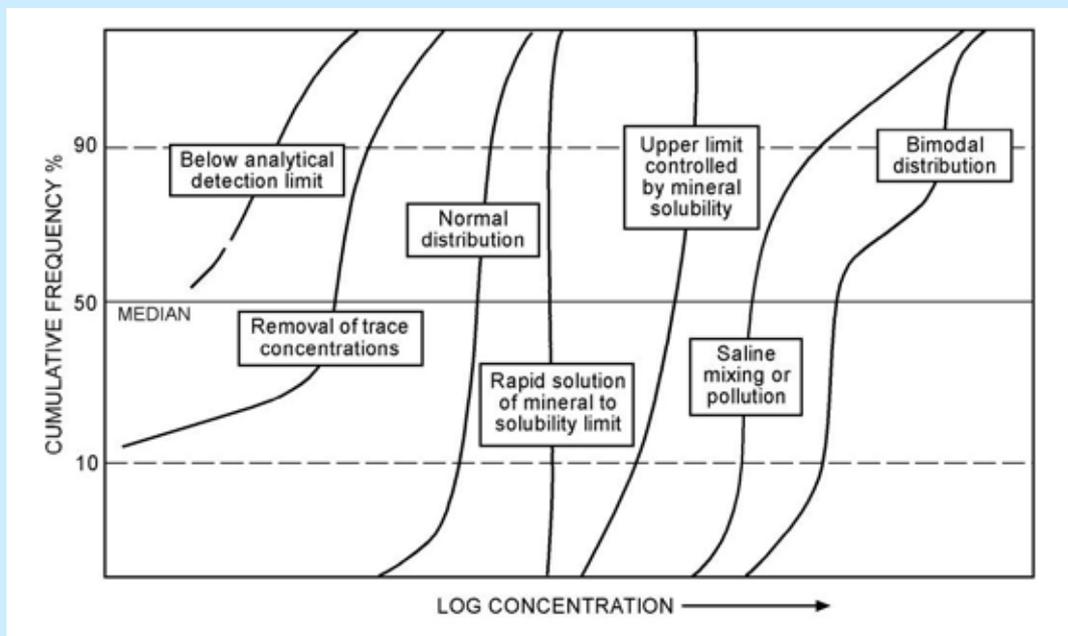
Table 5.1 Major and minor element data for groundwaters in the Plynlimon catchments.

	Units	River Severn Headwaters						River Wye Headwaters					
		Min.	Max.	Median	Mean	97.7 th %	N	Min.	Max.	Median	Mean	97.7 th %	N
T	°C	7.0	11.8	9.0	9.2	11.6	23	6.1	9.1	8.6	8.11	9.1	17
pH		4.91	8.83	6.04	6.26	8.52	23	4.63	7.84	6.13	6.13	7.76	18
Eh	MV	-79	514	411	297	505	12	65	410	242	224	387	15
DO	mg l ⁻¹	<0.1	10.2	3.9	3.92	10.0	23	<0.1	8.34	1.08	2.07	7.65	16
SEC	µS cm ⁻¹	54	328	101	150	326	23	32	319	86	129	308	18
δ ² H	‰	-42.3	-38.4	-40.9	-40.7	-38.6	12						
δ ¹⁸ O	‰	-10.5	-5.5	-6.6	-6.8	-6.0	23						
δ ¹³ C	‰	-24.1	-17.6	-20.5	-21.2	-18.0	12						
Ca	mg l ⁻¹	1.5	35.9	4.1	9.0	32.6	23	0.5	37.8	5.9	11.8	36.5	19
Mg	mg l ⁻¹	0.6	11.9	1.8	3.0	9.4	23	0.5	14.2	2.3	5.1	14.2	19
Na	mg l ⁻¹	4.2	69.4	5.9	13.9	66.4	23	3.5	14.4	5.0	5.8	12.9	19
K	mg l ⁻¹	<0.5	6	<0.5	1.3	5.5	23	0.1	1.9	0.3	0.5	1.8	19
Cl	mg l ⁻¹	5.0	12.5	7.1	7.7	12.1	23	3.7	7.2	5.1	5.2	6.6	19
SO ₄	mg l ⁻¹	3.0	23.6	7.5	9.6	19.8	23	<3	24	9	10.0	22.8	19
HCO ₃	mg l ⁻¹	<2	180	20	54	171	23	<3	149	<3	45	144	14
NO ₃ -N	mg l ⁻¹	<0.01	1.90	0.05	0.51	1.85	23	<0.01	0.97	0.02	0.09	0.64	19
NO ₂ -N	µg l ⁻¹	<3	49	<3	10	40	12	<3	25	<3	2	17	19
NH ₄ -N	µg l ⁻¹	<10	190	10	40	150	23	<20	663	20	77	495	19
P	µg l ⁻¹	10	63	21	28.2	62.2	12	10	330	10	63	327	19
DOC	mg l ⁻¹							0.22	7.30	1.05	1.32	5.15	19
F	mg l ⁻¹	0.005	0.4	0.05	0.09	0.36	23						
Br	µg l ⁻¹	12	143	30	30	90	23	7	61	20	23	53	19
I	µg l ⁻¹	1	10	2	2	8	23						
Si	mg l ⁻¹	1.08	7.89	2.79	3.27	6.51	23	0.45	7.37	3.07	4.00	7.28	19

Table 5.2 Trace element data for groundwaters in the Plynlimon catchments.

	River Severn Headwaters						River Wye Headwaters						
	Minimum	Maximum	Median	Mean	97.7th %	N	Minimum	Maximum	Median	Mean	97.7th %	N	
Ag	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	12	<0.05	<0.05	<0.05	<0.05	<0.05	19
Al	µg l ⁻¹	2	394	61	81	383	23	5	344	44	89	311	19
As	µg l ⁻¹	<1	3.0	<1	1.1	3.0	12	<0.5	8.0	0.5	1.6	7.8	19
Au	µg l ⁻¹	<0.05	0.13	<0.05	<0.05	0.13	12	<0.05	<0.05	<0.05	<0.05	<0.05	19
B	µg l ⁻¹	<20	165	<20	36	159	23	<20	56	<20	<20	50	19
Ba	µg l ⁻¹	3.0	33.2	5.2	8.0	25.1	23	1.1	9.3	3.3	4.0	8.9	19
Be	µg l ⁻¹	<0.05	0.44	0.06	0.09	0.34	23	<0.05	0.08	<0.05	0.04	0.08	19
Bi	µg l ⁻¹	<0.05	0.07	<0.05	<0.05	<0.05	23	<0.05	<0.05	<0.05	<0.05	<0.05	19
Cd	µg l ⁻¹	<0.05	1.76	<0.05	0.19	1.40	23	<0.05	0.15	0.07	0.08	0.14	19
Ce	µg l ⁻¹	<0.01	0.18	0.08	0.08	0.17	12	<0.01	0.20	0.03	0.04	0.18	19
Co	µg l ⁻¹	0.02	9.31	2.66	3.10	9.13	23	0.12	37.13	1.85	4.21	24.91	19
Cr	µg l ⁻¹	<0.5	83.9	<0.5	4.6	45.6	23	<0.5	<0.5	<0.5	<0.5	<0.5	19
Cs	µg l ⁻¹	<0.01	4.48	0.39	1.07	4.41	23	0.02	1.90	0.11	0.28	1.41	19
Cu	µg l ⁻¹	0.4	24.8	1.6	4.2	18.9	23	0.2	9.9	0.7	1.5	7.3	19
Dy	µg l ⁻¹	<0.01	0.33	0.04	0.06	0.26	12	<0.01	0.09	0.01	0.02	0.08	19
Er	µg l ⁻¹	<0.01	0.24	0.03	0.05	0.19	12	<0.01	0.05	0.01	0.01	0.05	19
Eu	µg l ⁻¹	<0.01	0.05	0.01	0.01	0.04	12	<0.01	0.01	<0.01	<0.01	0.01	19
Fe	mg l ⁻¹	<0.005	7.061	0.049	0.583	4.596	23	<0.005	12.068	0.286	1.704	10.017	19
Ga	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	23	<0.05	<0.05	<0.05	<0.05	<0.05	19
Gd	µg l ⁻¹	<0.01	0.26	0.05	0.06	0.21	12	<0.01	0.10	0.02	0.03	0.09	19
Ge	µg l ⁻¹	<0.05	0.53	<0.05	0.06	0.47	23	<0.05	0.14	<0.05	<0.05	0.09	19
Hf	µg l ⁻¹	<0.02	<0.02	<0.02	<0.02	<0.02	12	<0.02	<0.02	<0.02	<0.02	<0.02	19
Hg	µg l ⁻¹	<0.1	0.8	0.1	0.2	0.7	12	<0.1	<0.1	<0.1	<0.1	<0.1	19
Ho	µg l ⁻¹	<0.01	0.08	0.01	0.01	0.06	12	<0.01	0.02	<0.01	<0.01	0.02	19
In	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	0.01	12	<0.01	<0.01	<0.01	<0.01	<0.01	19
Ir	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	12	<0.05	<0.05	<0.05	<0.05	<0.05	19
La	µg l ⁻¹	<0.01	0.25	0.02	0.05	0.23	23	<0.01	0.07	0.01	0.01	0.05	19
Li	µg l ⁻¹	1.6	32.0	6.5	9.9	29.5	23	0.6	13.2	3.4	4.8	13.0	19
Lu	µg l ⁻¹	<0.01	0.03	<0.01	<0.01	0.02	12	<0.01	0.01	<0.01	<0.01	0.01	19
Mn	mg l ⁻¹	0.009	0.700	0.091	0.144	0.532	23	0.008	1.765	0.438	0.589	1.635	19
Mo	µg l ⁻¹	<0.1	2.2	<0.1	0.2	1.5	23	<0.1	3.5	0.2	0.5	3.0	19
Nb	µg l ⁻¹	<0.01	0.01	<0.01	<0.01	0.01	12	<0.01	0.01	<0.01	<0.01	<0.01	19
Nd	µg l ⁻¹	0.01	0.32	0.12	0.12	0.29	12	<0.01	0.14	0.03	0.04	0.14	19
Ni	µg l ⁻¹	<0.2	14.8	3.6	4.8	13.4	23	1.0	20.3	4.3	5.4	16.4	19
Os	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	12	<0.05	<0.05	<0.05	<0.05	<0.05	19
Pb	µg l ⁻¹	<2	10.0	<2	<2	7.5	23	<0.1	2.5	0.4	0.5	2.2	19
Pd	µg l ⁻¹	<0.2	<0.2	<0.2	<0.2	<0.2	12	<0.2	<0.2	<0.2	<0.2	<0.2	19
Pr	µg l ⁻¹	<0.01	0.04	0.02	0.02	0.04	12	<0.01	0.03	<0.01	<0.01	0.03	19
Pt	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	12	<0.01	<0.01	<0.01	<0.01	<0.01	19
Rb	µg l ⁻¹	0.1	11.3	1.0	2.8	10.7	23	0.2	4.6	0.6	1.1	4.5	19
Re	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	12	<0.01	<0.01	<0.01	<0.01	<0.01	19
Rh	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	12	<0.01	<0.01	<0.01	<0.01	<0.01	19
Ru	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	12	<0.05	<0.05	<0.05	<0.05	<0.05	19
Sb	µg l ⁻¹	<0.05	0.49	<0.05	0.08	0.47	23	<0.05	0.48	<0.05	0.09	0.45	19
Sc	µg l ⁻¹	0	2	1	1	2	12	<1	<1	<1	<1	<1	19
Se	µg l ⁻¹	<0.5	<0.5	<0.5	<0.5	<0.5	12	<0.5	<0.5	<0.5	<0.5	<0.5	19
Sm	µg l ⁻¹	<0.05	0.13	<0.05	0.04	0.11	12	<0.05	0.06	<0.05	<0.05	0.06	19
Sn	µg l ⁻¹	0.08	2.31	0.18	0.35	1.81	12	<0.05	2.23	0.07	0.19	1.39	19
Sr	µg l ⁻¹	8	124	30	34	119	23	2	146	9	24	123	19
Ta	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	12	<0.02	<0.02	<0.02	<0.02	<0.02	19
Tb	µg l ⁻¹	<0.01	0.06	0.01	0.01	0.05	8	<0.01	0.01	<0.01	<0.01	0.01	19
Te	µg l ⁻¹	<0.05	0.19	<0.05	0.06	0.17	12	<0.05	<0.05	<0.05	<0.05	<0.05	19
Th	µg l ⁻¹	<0.05	0.27	0.07	0.09	0.24	12	<0.05	<0.05	<0.05	<0.05	<0.05	19
Ti	µg l ⁻¹	<10	<10	<10	<10	<10	12	<10	<10	<10	<10	<10	19
Tl	µg l ⁻¹	<0.01	0.07	0.01	0.02	0.07	23	<0.01	0.02	<0.01	<0.01	0.02	19
Tm	µg l ⁻¹	<0.01	0.04	<0.01	<0.01	0.03	12	<0.01	0.01	<0.01	<0.01	0.01	19
U	µg l ⁻¹	<0.02	1.11	0.03	0.13	1.01	23	<0.02	0.74	0.02	0.09	0.57	19
V	µg l ⁻¹	<1	<1	<1	<1	<1	12	<0.2	<0.2	<0.2	<0.2	<0.2	19
W	µg l ⁻¹	<0.1	0.10	<0.1	<0.1	0.10	12	<0.02	<0.02	<0.02	<0.02	<0.02	19
Y	µg l ⁻¹	0.03	1.41	0.19	0.32	1.30	23	0.01	0.47	0.08	0.12	0.41	19
Yb	µg l ⁻¹	<0.01	0.22	0.03	0.04	0.18	12	<0.01	0.05	0.01	0.01	0.05	19
Zn	µg l ⁻¹	1	129	13	29	125	23	<0.5	30	9	11	30	18
Zr	µg l ⁻¹	<0.1	0.60	<0.1	0.10	0.47	11	<0.02	0.16	<0.02	0.03	0.16	19
DON	mg l ⁻¹							0.160	1.53	0.35	0.41	1.28	19

Box 5.1. Use of cumulative frequency diagrams to indicate baseline characteristics in groundwaters



- i) The median and upper and lower percentile concentrations are used as a reference for the element baseline which can be compared regionally or in relation to other elements.
- ii) Normal to multi-modal distributions are to be expected for many elements reflecting the range in recharge conditions, water-rock interaction and residence times under natural aquifer conditions.
- iii) Narrow ranges of concentration may indicate rapid attainment of saturation with minerals (e.g. Si with silica, Ca with calcite).
- iv) A strong negative skew may indicate selective removal of an element by some geochemical process (e.g. NO_3 by *in situ* denitrification).
- v) A narrow range in concentration at the upper limit may indicate a mineral solubility control (e.g. F by fluorite)
- vi) A positive skew most probably indicates a contaminant source for a small number of the groundwaters and this gives one simple way of separating those waters above the baseline. Alternatively the highest concentrations may indicate waters of natural higher salinity.

5.2.2 Major elements

Major element data for the Severn and Wye headwater catchments are shown on Table 5.1. The median concentrations are similar for both catchments for most major elements. Higher Na and Cl in the forested Severn catchment may be a function of increased evaporation or scavenging of sea-salts. The Severn catchment also has slightly higher median HCO_3 and P, whilst the Wye catchment has slightly higher Ca, Mg and SO_4 , possibly derived from previous mining activities.

The data are presented as boxplots and cumulative probability plots on Figures 5.2 and 5.3. The solid line on the boxplots (Figure 5.2) represent a dilute seawater line, normalised to the median Cl of the dataset. Chloride concentrations show a very narrow range, particularly in the Wye catchment. The enhancement of Na and the other solutes above this line (Figure 5.2) indicates inputs additional to rainfall. The cumulative frequency plots (Figure 5.3) show that bicarbonate is the dominant anion in about half of the samples. The HCO_3 and SO_4 profiles indicate two populations, possibly with mixing between them. A separate population exists for Na (Figure 5.3), representing the Na- HCO_3 waters shown on the Piper plot (Figure 5.1).

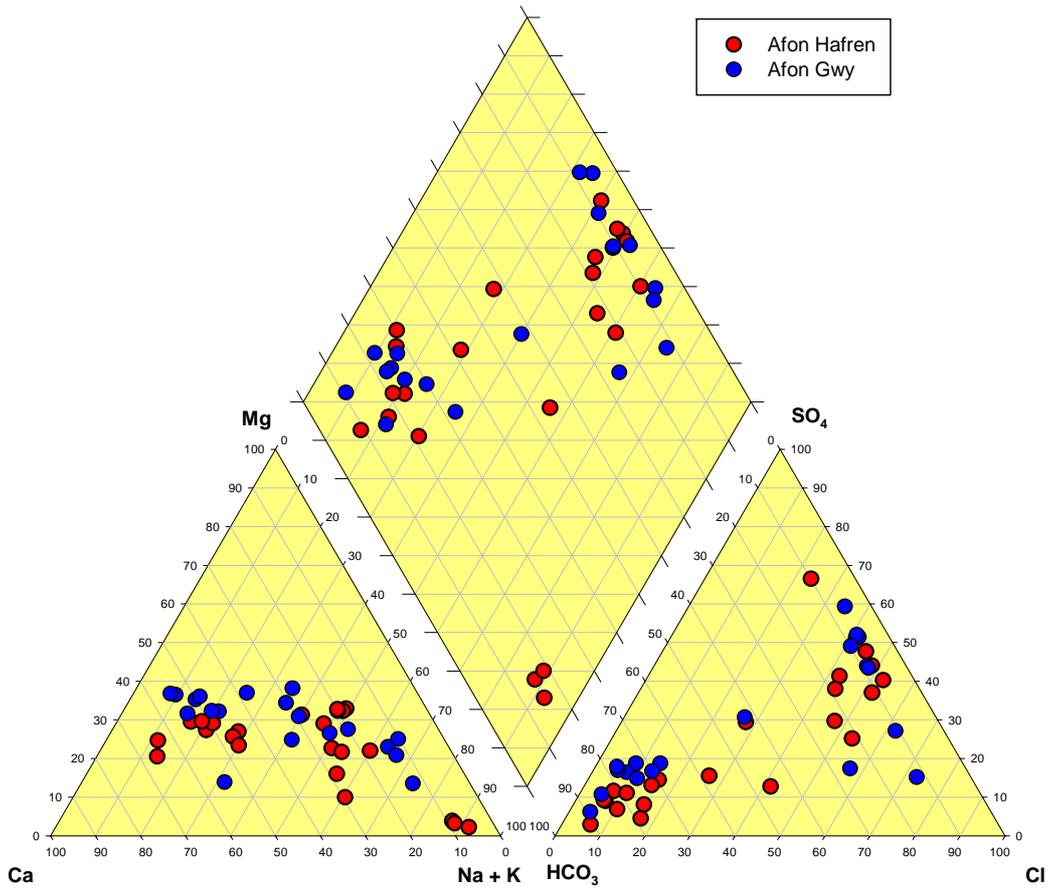


Figure 5.1 PIPER plot showing the relative proportions of major elements in the groundwaters of the Plynlimon catchments of Severn (Afon Hafren) and Wye (Afon Gwy).

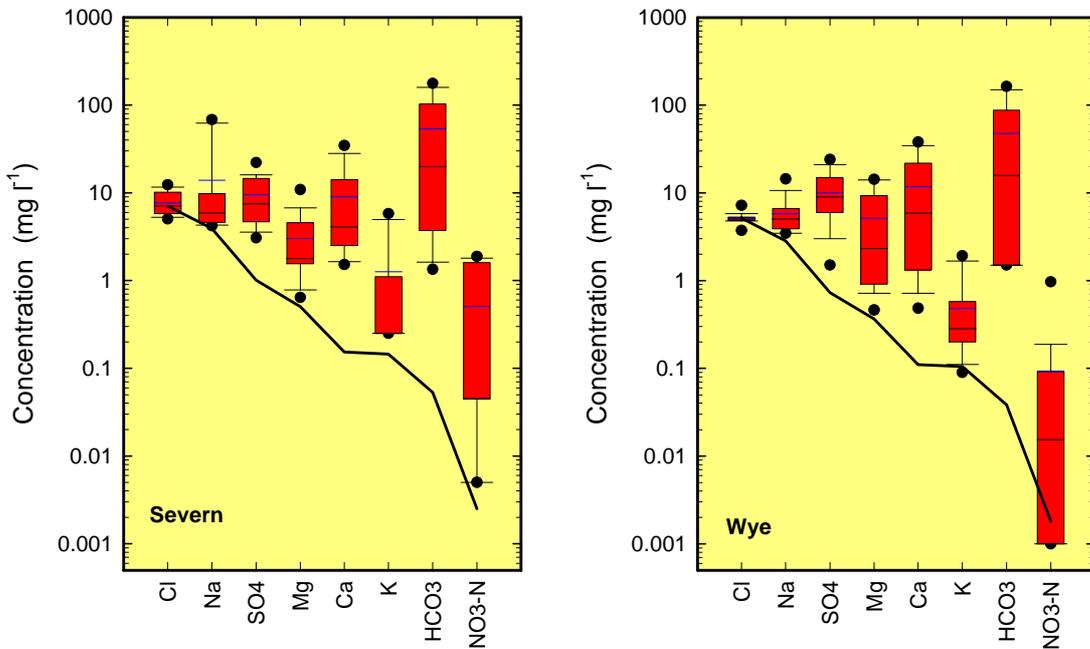


Figure 5.2 Boxplots for major and minor elements in the Severn (Afon Hafren) and Wye (Afon Gwy) Plynlimon catchments.

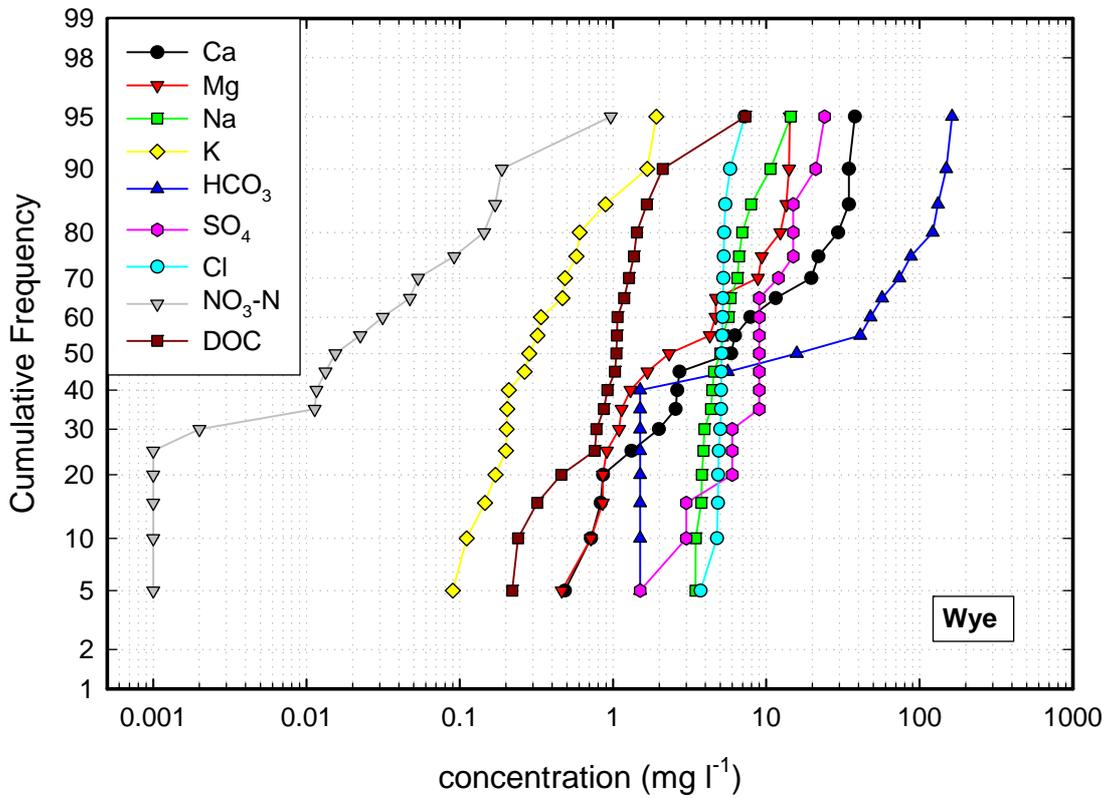
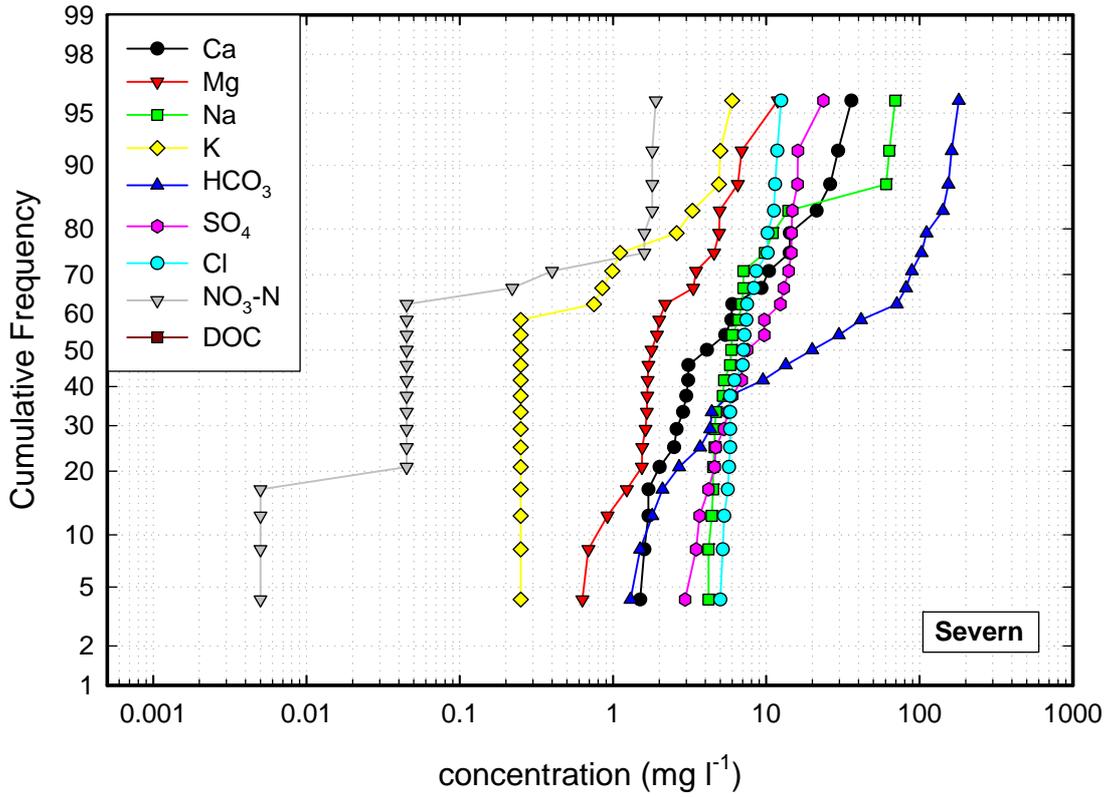


Figure 5.3 Cumulative probability plots for major and minor elements in groundwaters of the Severn (Afon Hafren) and Wye (Afon Gwy) Plynlimon catchments.

Nitrate concentrations vary from less than the limit of detection up to 1-2 mg l⁻¹ and NH₄ is present at up to 0.7 mg l⁻¹ in the more reducing groundwaters. The dominant form of N in the Wye groundwaters is dissolved organic nitrogen (DON) with concentrations up to 1.53 mg l⁻¹.

5.2.3 *Minor and trace elements*

Minor and trace element summary data are shown on Tables 5.1 and 5.2 and presented as boxplots and cumulative probability plots on Figures 5.4 and 5.5. The halogen elements Br and I are present at low concentrations reflecting the low salinity of these waters. Fluoride concentrations in the Severn groundwaters are generally low. The highest concentrations are present in groundwaters from only one part of the catchment reflecting a local source. The median for total dissolved P is slightly higher in the Severn groundwaters (Table 5.1) and correlates with F. However the highest concentrations were present in the Wye, up to 330 µg l⁻¹.

The majority of trace elements are similar in both catchments, although there is a tendency for slightly higher median concentrations of metals in the Severn catchment. Most trace metals are present at low concentrations, the exceptions being Al, Mn and Fe. The median for aluminium is higher in the forested Severn catchment, a feature also noted in stream waters of these catchments (Shand et al., 2005). The Wye groundwaters have a tendency for higher concentrations of Fe and especially Mn.

5.3 **Teifi groundwaters**

The summary data for the Afon Teifi groundwaters is shown in Table 5.3 for major and minor solutes and Table 5.4 for trace elements. The groundwaters of the Teifi have been sub-divided on the basis of lithology into superficial deposit groundwaters and bedrock +/- superficial deposit groundwaters. In the latter case, most boreholes are likely to be dominated by bedrock, but insufficient details were available to characterise them fully. The boreholes and wells depths vary from 5 m to ca. 100 m.

5.3.1 *Water types and physicochemical characteristics*

Groundwater temperatures vary from 4 to 12 °C (Table 5.3), the lower temperatures reflecting either very shallow flow or sampling from storage tanks. Typical temperatures are 8-11 °C. The range in pH is relatively large, from acidic (minimum pH 5.2), mainly in shallow groundwaters, to slightly alkaline (maximum pH 7.6). The SEC also varies from very fresh (117 µS cm⁻¹) to moderately mineralised (556 µS cm⁻¹). Redox measurements (Eh and DO) in the bedrock group groundwaters indicate that the groundwaters vary from oxidising to slightly reducing (Eh from 291 to 556 mV). However, many sources were pumped via storage tanks and redox measurements may have been modified e.g. through contact with air. The superficial deposit groundwaters sampled were all oxidising (Eh from 410 to 432 mV).

On a Piper plot (Figure 5.6), the groundwaters vary from Ca-HCO₃ type to mixed types. The groundwaters from the two groups show significant overlap, but groundwaters within the superficial deposits group tend to be more enriched in HCO₃ relative to Cl. For the bedrock groundwaters, there is a tendency for the lower TDS and lower pH groundwaters to be more dominated by Na-Cl-SO₄ types.

5.3.2 *Major elements*

Major element data for the groundwaters are shown on Table 5.3. The median concentrations are similar for both groups, but the superficial deposit groundwaters have higher median SEC and concentrations of major elements. The bedrock groundwater group shows a much wider range of concentrations, but this is based on only a small number of samples.

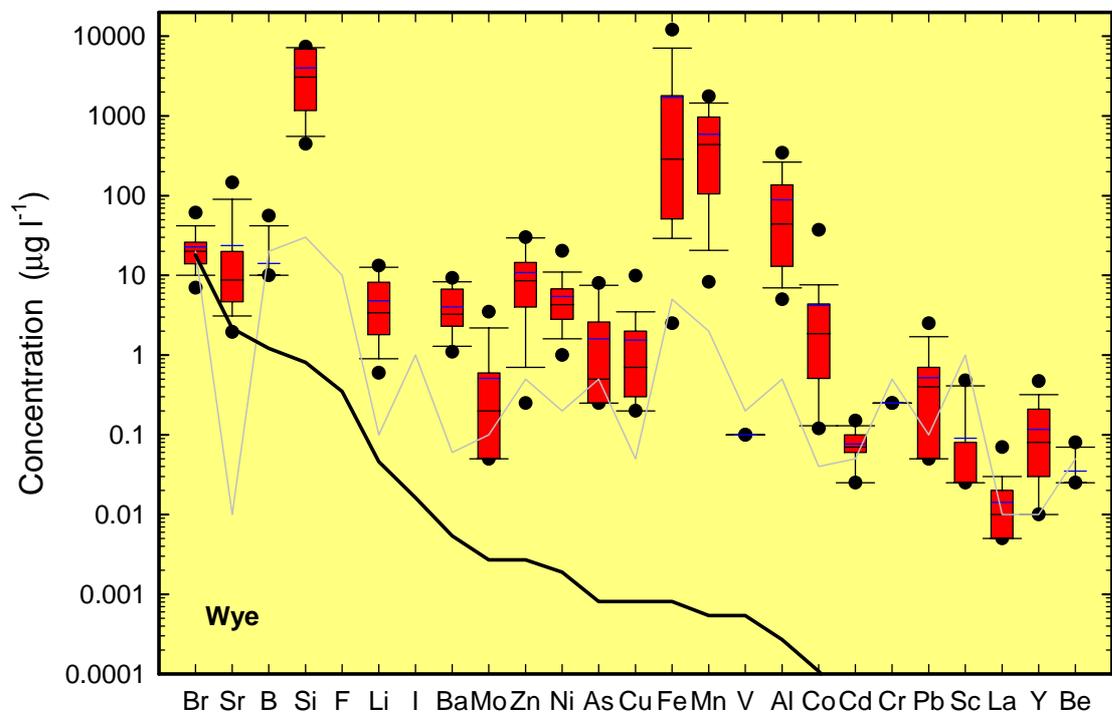
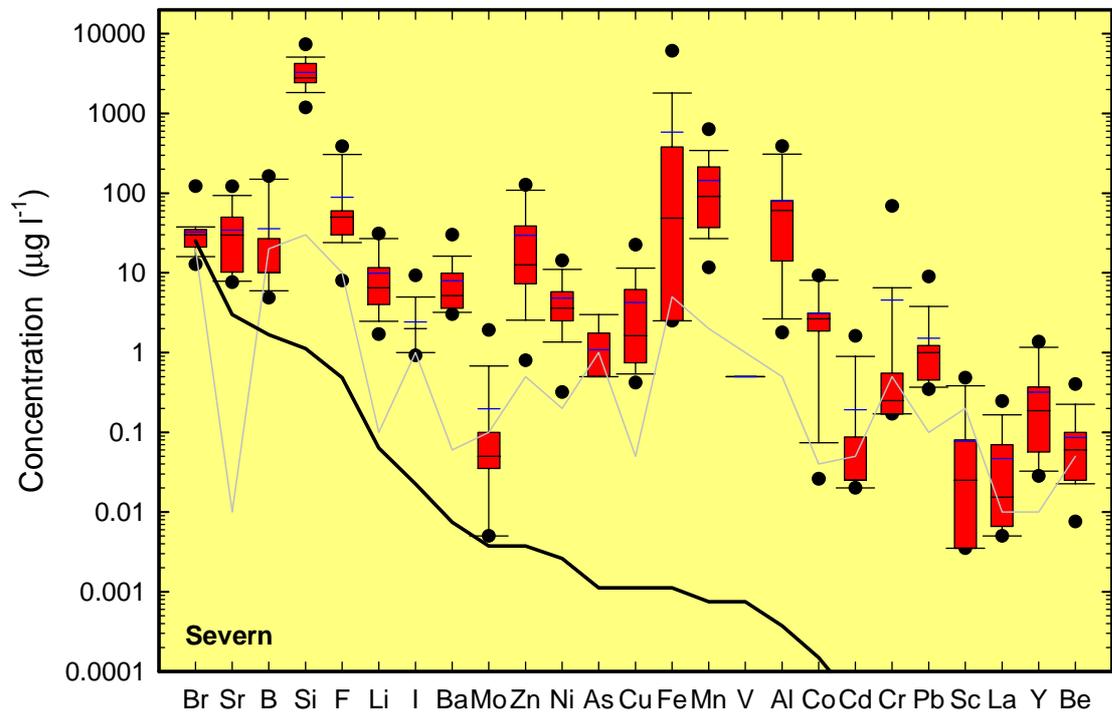


Figure 5.4 Boxplots for minor and trace elements in the Severn (Afon Hafren) and Wye (Afon Gwy) Plynlimon catchments.

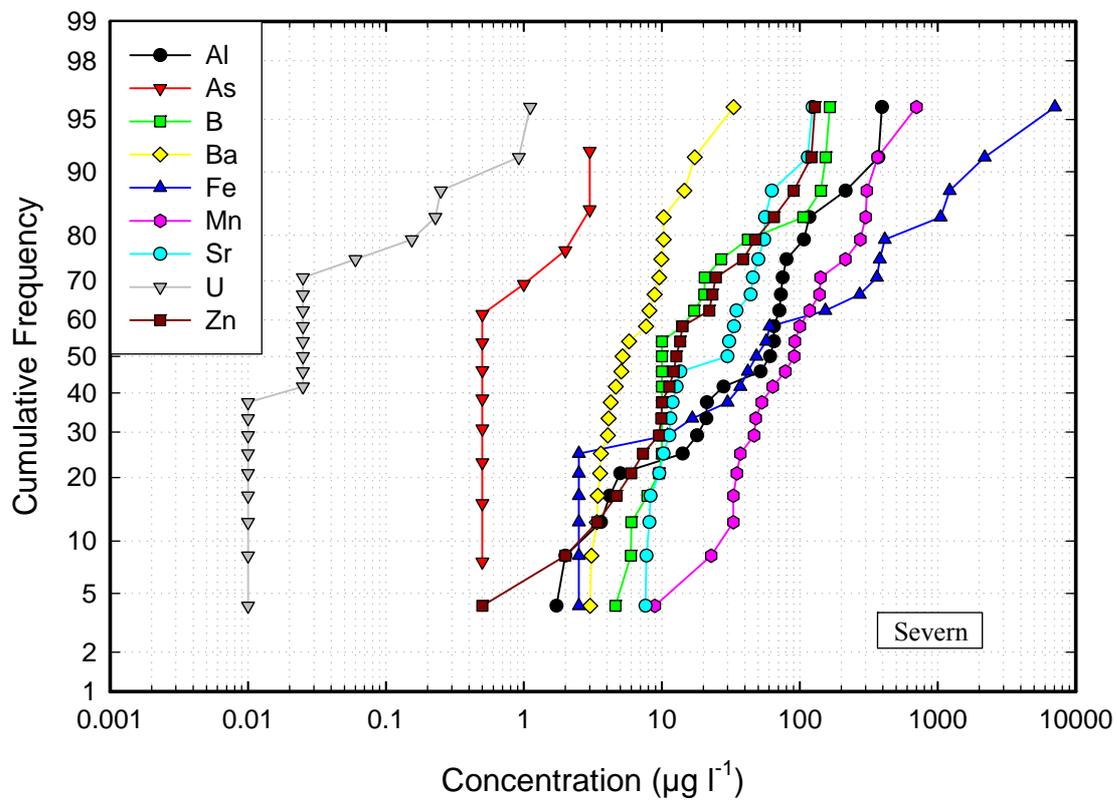
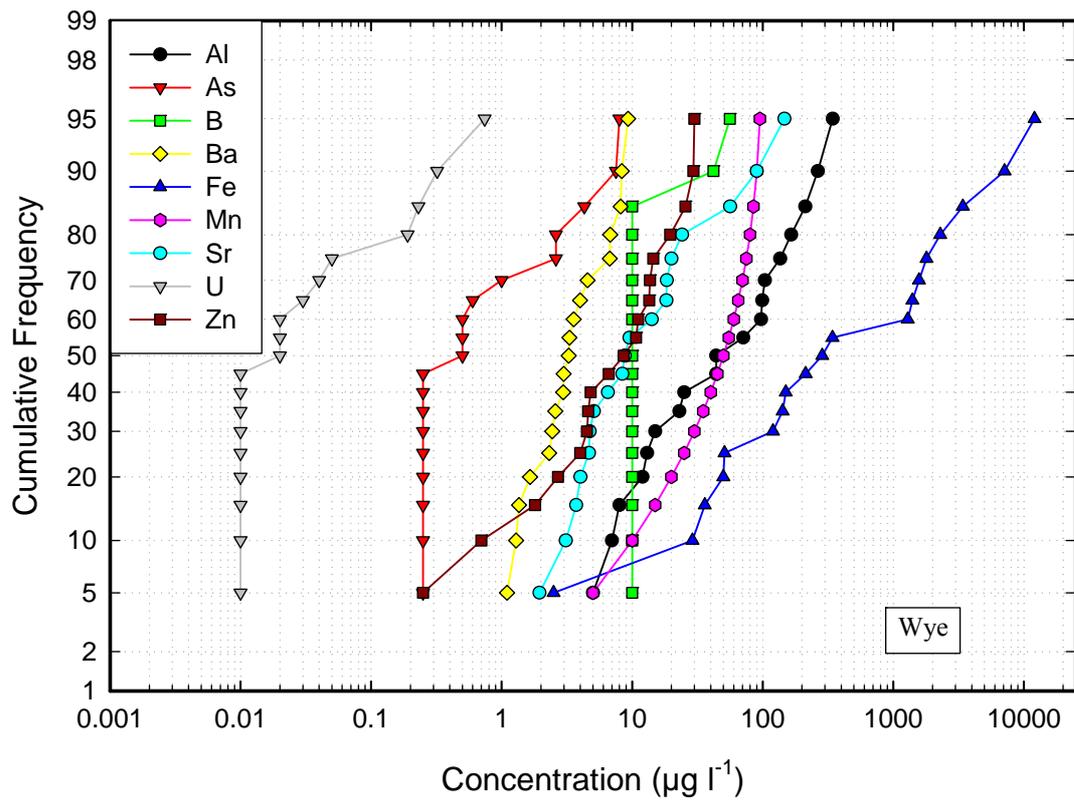


Figure 5.5 Cumulative probability plots for trace elements in groundwaters of the Severn (Afon Hafren) and Wye (Afon Gwy) Plynlimon catchments.

Table 5.3 Major and minor element data for groundwaters in the Teifi catchment.

	Units	Bedrock +/- Drift						Drift					
		Min.	Max.	Median	Mean	97.7 th %	N	Min.	Max.	Median	Mean	97.7 th %	N
T	°C	4.4	11.5	9.6	9.5	11.4	48	9.5	11.1	10.4	10.3	11.0	6
pH		5.16	7.50	6.47	6.46	7.30	48	6.33	7.55	6.86	6.87	7.52	6
Eh	mV	291	556	449	446	555	33	410	432	429	425	432	4
DO	mg l ⁻¹	<0.1	10.9	6.2	6.1	10.9	44	1.5	7.7	4.7	4.7	7.5	4
SEC	µS cm ⁻¹	117	662	226	262	613	48	228	572	333	368	562	6
δ ² H	‰	-42.0	-33.0	-38.0	-37.6	-33.0	11						
δ ¹⁸ O	‰	-6.6	-5.7	-6.2	-6.2	-5.7	11						
Ca	mg l ⁻¹	6.5	65.5	18.0	22.6	59.2	48	16.5	83.1	43.9	47.6	82.0	6
Mg	mg l ⁻¹	2.2	17.6	4.4	5.9	15.4	48	4.7	12.6	7.7	7.9	12.1	6
Na	mg l ⁻¹	5.4	51.5	11.9	13.9	34.6	48	9.4	23.0	17.0	15.8	22.5	6
K	mg l ⁻¹	0.4	33.7	1.3	3.0	16.8	48	0.8	2.1	1.2	1.3	2.1	6
Cl	mg l ⁻¹	11.4	92.0	21.3	25.3	63.1	48	12.6	44.7	26.7	27.1	43.4	6
SO ₄	mg l ⁻¹	4.2	41.2	11.6	13.6	32.1	48	12.3	28.3	15.2	18.2	27.9	6
HCO ₃	mg l ⁻¹	7	291	27	52	229	48	34	176	119	109	173	6
NO ₃ -N	mg l ⁻¹	<0.09	9.33	0.95	1.47	7.01	48	0.54	4.34	1.99	2.27	4.27	6
NH ₄ -N	µg l ⁻¹	<10	1720	<10	72	769	48	<10	70	30	33	69	6
P	µg l ⁻¹	10	1670	45	123	906	47	23	173	55	73	164	6
TOC	mg l ⁻¹	0.43	6.96	1.32	1.87	6.00	34	0.56	1.02	0.89	0.82	1.01	3
F	mg l ⁻¹	0.03	0.23	0.06	0.08	0.19	48	0.07	0.19	0.09	0.10	0.18	6
Br	µg l ⁻¹	20	217	81	93	210	48	52	149	104	104	147	6
I	µg l ⁻¹	1	25	3	5	19	48	1	10	6	6	10	6
Si	mg l ⁻¹	1.49	7.41	2.56	3.09	6.92	48	3.01	5.90	3.47	3.87	5.70	6

		Teifi Valley bedrock +/-Superficial deposits						Superficial deposits					
		Minimum	Maximum	Median	Mean	97.7th %	N	Minimum	Maximum	Median	Mean	97.7th %	N
Ag	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	48	<0.05	<0.05	<0.05	<0.05	<0.05	6
Al	µg l ⁻¹	7	628	34	74	532	48	6	63	13	22	59	6
As	µg l ⁻¹	<0.5	7.2	0.5	0.9	3.7	48	<0.5	1.1	0.6	0.6	1.1	6
Au	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	47	<0.05	<0.05	<0.05	<0.05	<0.05	6
B	µg l ⁻¹	<20	129	<20	<20	43	48	<20	24	<20	12	22	6
Ba	µg l ⁻¹	1.2	159.3	6.4	10.8	27.3	48	1.0	39.7	23.0	21.7	39.4	6
Be	µg l ⁻¹	<0.05	0.18	<0.05	<0.05	0.15	48	<0.05	0.08	<0.05	<0.05	0.07	6
Bi	µg l ⁻¹	<0.05	0.26	<0.05	<0.05	<0.05	48	<0.05	<0.05	<0.05	<0.05	<0.05	6
Cd	µg l ⁻¹	0.03	0.25	0.03	0.04	0.12	48	<0.05	0.06	0.03	0.03	0.06	6
Ce	µg l ⁻¹	0.01	0.70	0.04	0.10	0.65	48	<0.01	0.03	0.01	0.01	0.03	6
Co	µg l ⁻¹	<0.02	5.51	0.13	0.43	4.40	48	<0.02	0.73	0.04	0.15	0.65	6
Cr	µg l ⁻¹	<0.5	2.7	0.6	0.6	1.9	48	<0.5	1.9	0.8	0.9	1.9	6
Cs	µg l ⁻¹	0.01	2.26	0.11	0.25	1.30	48	<0.01	0.39	0.03	0.10	0.36	6
Cu	µg l ⁻¹	0.5	730.0	2.6	24.6	121.2	48	0.8	4.7	1.8	2.3	4.6	6
Dy	µg l ⁻¹	<0.01	0.84	0.04	0.08	0.42	48	<0.01	0.01	<0.01	<0.01	0.01	6
Er	µg l ⁻¹	<0.01	0.43	0.02	0.05	0.22	48	<0.01	<0.01	<0.01	<0.01	<0.01	6
Eu	µg l ⁻¹	<0.01	0.24	0.01	0.03	0.14	48	<0.01	<0.01	<0.01	<0.01	<0.01	6
Fe	mg l ⁻¹	<0.006	0.718	0.014	0.054	0.467	48	<0.006	<0.006	<0.006	<0.006	<0.006	6
Ga	µg l ⁻¹	<0.05	0.14	<0.05	<0.05	0.11	48	<0.05	<0.05	<0.05	<0.05	<0.05	6
Gd	µg l ⁻¹	<0.01	1.12	0.05	0.13	0.75	48	<0.01	0.01	<0.01	<0.01	<0.01	6
Ge	µg l ⁻¹	<0.05	0.06	<0.05	<0.05	<0.05	48	<0.05	<0.05	<0.05	<0.05	<0.05	6
Hf	µg l ⁻¹	<0.02	0.03	<0.02	<0.02	0.02	47	<0.02	<0.02	<0.02	<0.02	<0.02	6
Hg	µg l ⁻¹	<0.1	0.2	<0.1	<0.1	0.1	47	<0.1	0.1	<0.1	<0.1	<0.1	6
Ho	µg l ⁻¹	<0.01	0.16	0.01	0.02	0.08	48	<0.01	<0.01	<0.01	<0.01	<0.01	6
In	µg l ⁻¹	<0.01	0.01	<0.01	<0.01	<0.01	47	<0.01	<0.01	<0.01	<0.01	<0.01	6
Ir	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	47	<0.05	<0.05	<0.05	<0.05	<0.05	6
La	µg l ⁻¹	<0.01	0.37	0.04	0.06	0.32	48	<0.01	0.02	0.01	0.01	0.02	6
Li	µg l ⁻¹	0.1	33.1	1.2	3.9	18.7	48	1.6	11.4	2.1	3.7	10.5	6
Lu	µg l ⁻¹	<0.01	0.06	<0.01	<0.01	0.03	48	<0.01	<0.01	<0.01	<0.01	<0.01	6
Mn	mg l ⁻¹	0.001	2.400	0.006	0.079	0.359	48	0.002	0.074	0.005	0.017	0.066	6
Mo	µg l ⁻¹	<0.1	6.1	0.1	0.4	2.1	48	<0.1	6.1	0.1	0.4	2.1	6
Nb	µg l ⁻¹	<0.01	0.02	<0.01	<0.01	0.02	47	<0.01	<0.01	<0.01	<0.01	<0.01	6
Nd	µg l ⁻¹	0.01	2.25	0.12	0.24	1.17	48	0.01	0.02	0.02	0.02	0.02	6
Ni	µg l ⁻¹	<0.2	11.3	3.5	3.0	7.5	48	<0.2	1.2	0.9	0.8	1.2	6
Os	µg l ⁻¹	<0.05	0.08	<0.05	<0.05	<0.05	47	<0.05	<0.05	<0.05	<0.05	<0.05	6
Pb	µg l ⁻¹	<0.1	6.1	0.4	0.7	3.6	48	<0.1	1.8	0.2	0.5	1.6	6
Pd	µg l ⁻¹	<0.2	<0.2	<0.2	<0.2	<0.2	47	<0.2	<0.2	<0.2	<0.2	<0.2	6
Pr	µg l ⁻¹	<0.01	0.34	0.01	0.03	0.15	48	<0.01	<0.01	<0.01	<0.01	<0.01	6
Pt	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	47	<0.01	<0.01	<0.01	<0.01	<0.01	6
Rb	µg l ⁻¹	0.2	18.7	1.1	1.9	10.8	48	0.2	4.6	0.3	1.1	4.1	6
Re	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	47	<0.01	<0.01	<0.01	<0.01	<0.01	6
Rh	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	47	<0.01	<0.01	<0.01	<0.01	<0.01	6
Ru	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	47	<0.05	<0.05	<0.05	<0.05	<0.05	6
Sb	µg l ⁻¹	<0.05	0.60	0.06	0.09	0.44	48	<0.05	<0.05	<0.05	<0.05	<0.05	6
Sc	µg l ⁻¹	<1	1	<1	<1	1	47	<1	1	<1	<1	<1	6
Se	µg l ⁻¹	<0.5	1.5	0.6	0.6	1.3	48	<0.5	1.0	0.9	0.8	1.0	6
Sm	µg l ⁻¹	<0.02	0.90	0.04	0.10	0.56	48	<0.02	<0.02	<0.02	<0.02	<0.02	6
Sn	µg l ⁻¹	<0.05	1.13	0.45	0.43	0.68	47	0.06	0.55	0.27	0.29	0.55	6
Sr	µg l ⁻¹	22	640	51	78	258	48	54	255	128	137	248	6
Ta	µg l ⁻¹	<0.02	<0.02	<0.02	<0.02	<0.02	47	<0.02	<0.02	<0.02	<0.02	<0.02	6
Tb	µg l ⁻¹	< 0.01	0.15	0.01	0.02	0.09	48	< .01	< .01	< .01	< .01	< .01	6
Te	µg l ⁻¹	< 0.05	< .05	< .05	< .05	< .05	47	< .05	< .05	< .05	< .05	< .05	6
Th	µg l ⁻¹	< 0.05	0.10	< .05	< .05	0.06	48	< .05	< .05	< .05	< .05	< .05	6
Ti	µg l ⁻¹	<10	<10	<10	<10	<10	47	<10	<10	<10	<10	<10	6
Tl	µg l ⁻¹	< 0.01	0.12	< .01	< .01	0.07	48	< .01	0.01	< .01	< .01	< .01	6
Tm	µg l ⁻¹	< 0.01	0.07	< .01	< .01	0.03	48	< .01	< .01	< .01	< .01	< .01	6
U	µg l ⁻¹	<0.02	7.93	0.02	0.26	0.81	48	0.02	0.39	0.09	0.13	0.37	6
V	µg l ⁻¹	<0.2	1.7	<0.2	0.3	1.4	48	<0.2	0.5	<0.2	0.2	0.5	6
W	µg l ⁻¹	<0.02	0.10	<0.02	<0.02	0.04	47	<0.02	<0.02	<0.02	<0.02	<0.02	6
Y	µg l ⁻¹	0.02	3.98	0.21	0.47	2.54	48	0.02	0.05	0.04	0.04	0.05	6
Yb	µg l ⁻¹	<0.01	0.38	0.02	0.04	0.17	48	<0.01	<0.01	<0.01	<0.01	<0.01	6
Zn	µg l ⁻¹	1	101	5	13	68	48	2	63	4	19	60	6
Zr	µg l ⁻¹	<0.02	1.00	0.03	0.10	0.78	47	<0.02	0.03	<0.02	<0.02	0.03	6

Table 5.4 Trace element data for groundwaters in the Teifi catchment.

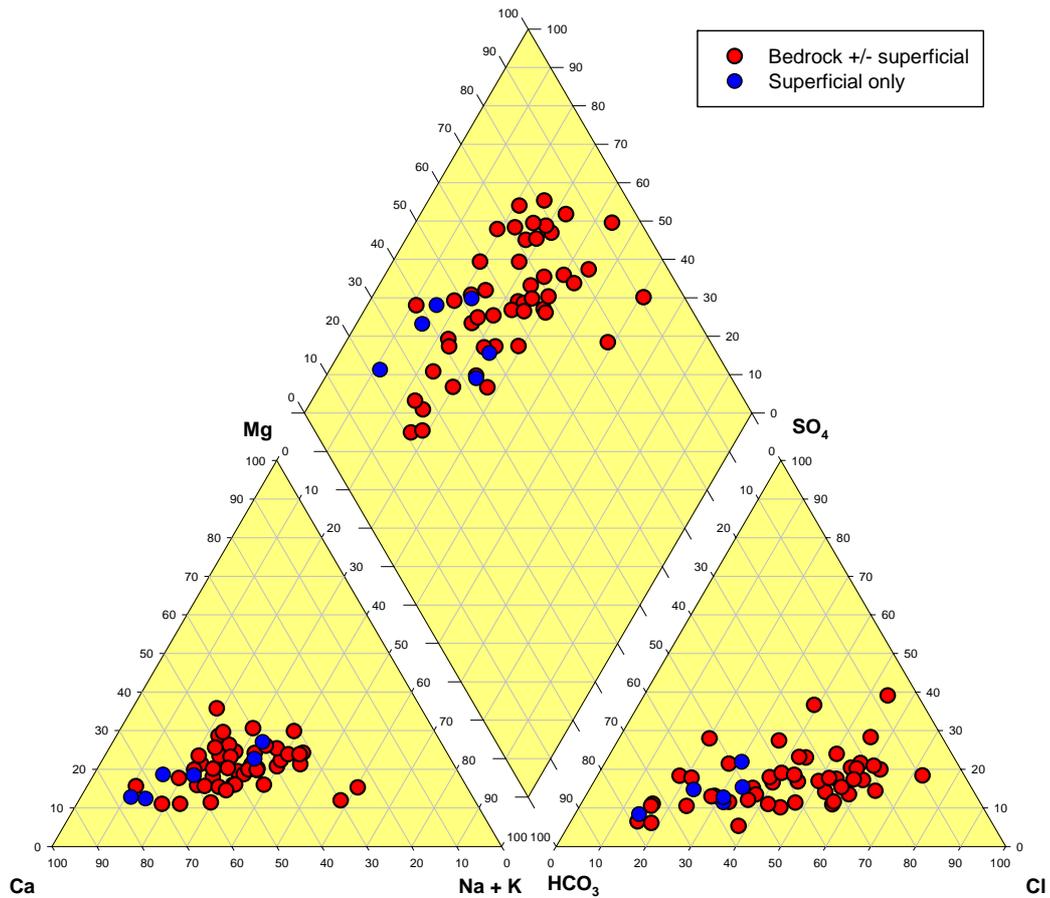


Figure 5.6 PIPER plot showing the relative proportions of major elements in the Teifi Valley groundwaters.

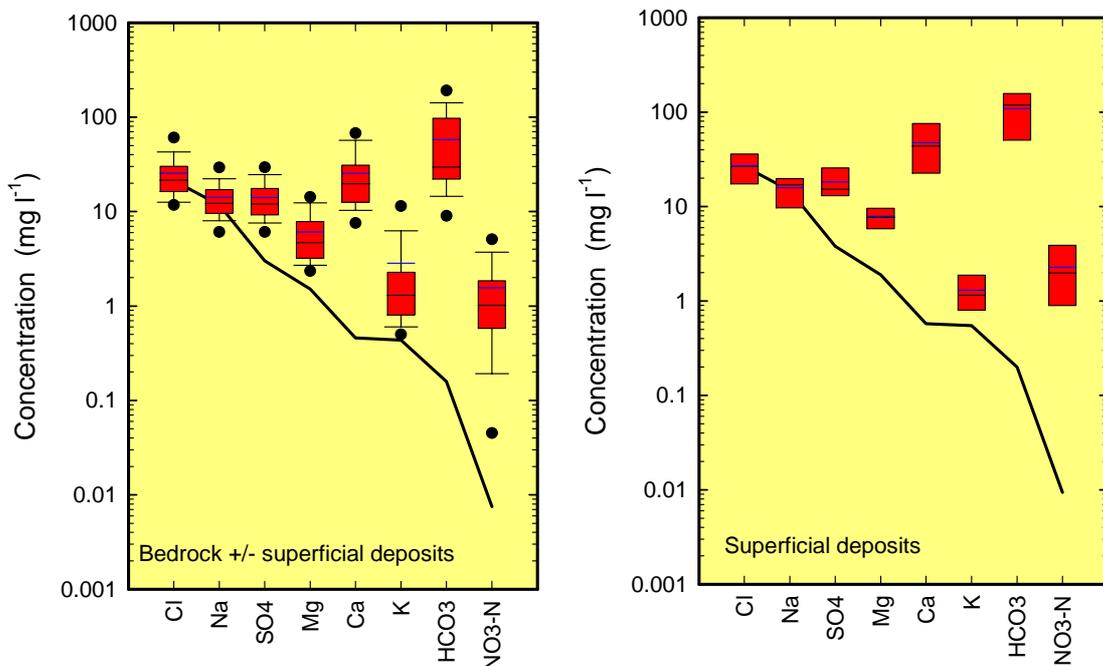


Figure 5.7 Boxplots for major and minor elements in groundwaters of the Teifi catchment.

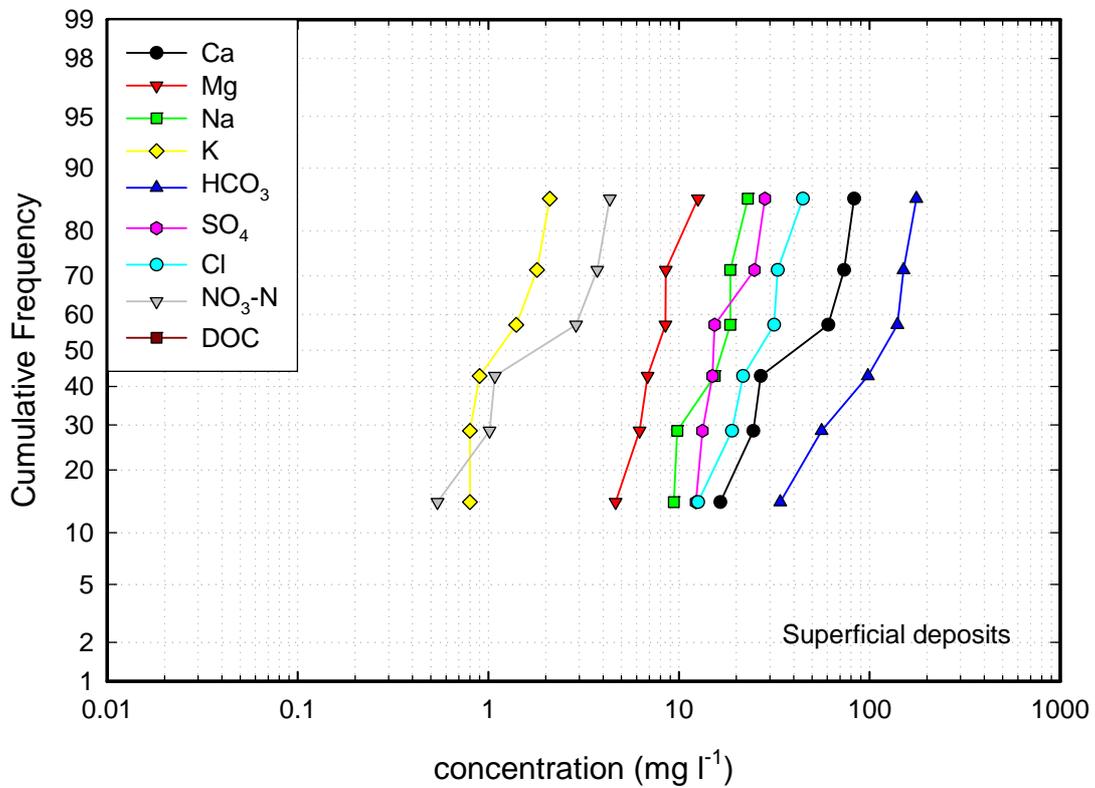
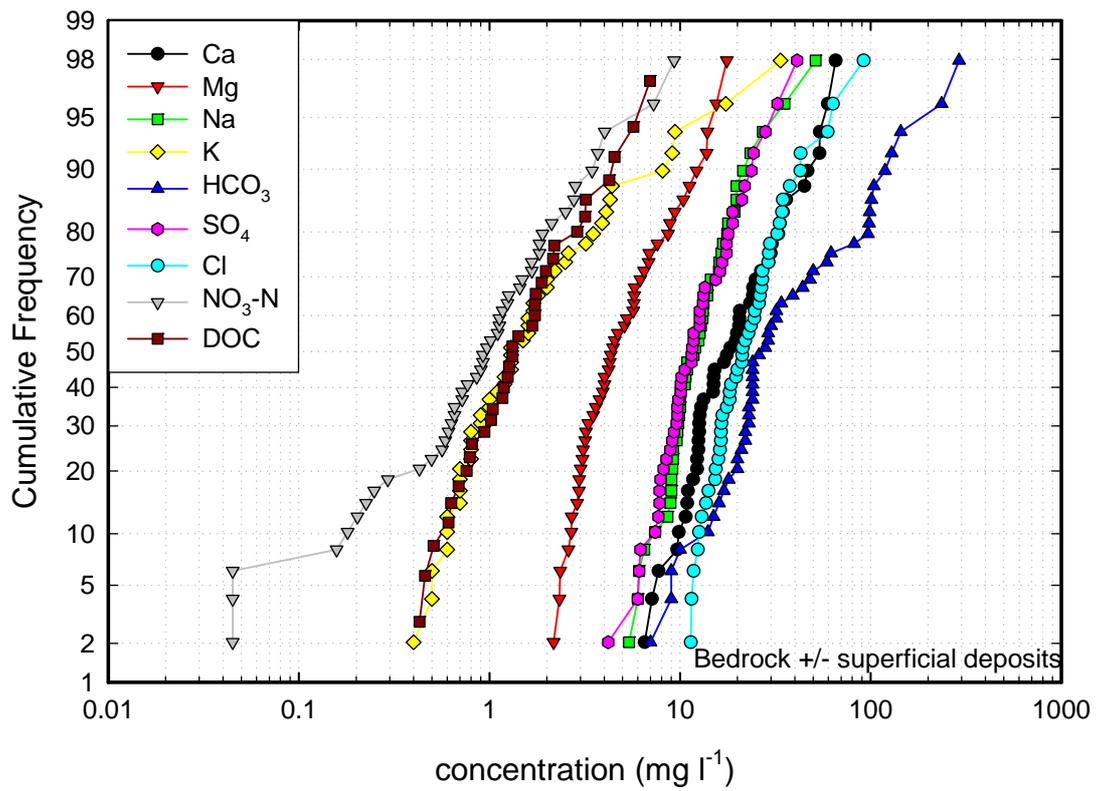


Figure 5.8 Cumulative probability plots for major and minor elements in groundwaters of the Teifi catchment.

The data are presented as boxplots and cumulative probability plots on Figures 5.7 and 5.8. The solid line on the boxplots represent a dilute seawater line, normalised to the median Cl of the dataset. Median Na concentrations plot close to the dilute seawater line, indicating little input from water-rock interaction. The other major elements plot significantly above this line, especially Ca and HCO₃. The cumulative frequency plots (Figure 5.8) show that most elements show a near log-normal distribution, but are skewed at high concentrations. This is particularly the case for K, which changes trend at ca. 5 mg l⁻¹ (similar to the upper baseline in the Severn groundwaters, Table 5.1). The bicarbonate plot shows that two populations exist, the highest starting at ca. 100 mg l⁻¹, and this is also present in the superficial data plot.

Nitrate concentrations vary in the bedrock groundwaters from less than the limit of detection up to 9.3 mg l⁻¹ and NH₄ is present at up to 1.72 mg l⁻¹. TOC concentrations may also reach moderately high concentrations, up to 7 mg l⁻¹.

5.3.3 *Minor and trace elements*

Minor and trace element summary data are shown on Figures 5.9 and 5.10 and summarised in Tables 5.3 and 5.4. The halogen elements Br and I are present at low concentrations reflecting the low salinity of these waters. Fluoride concentrations in the Teifi groundwaters are generally low. The median concentrations for total dissolved P is similar in the drift and superficial deposit groundwaters, but locally high concentrations occur in both types (with up to 1670 µg l⁻¹ in the bedrock group).

The majority of trace elements are similar in both catchments, although the concentrations of Fe, Mn, Al and Ni are higher in the bedrock group. Aluminium concentrations show little relationship with pH and it is possible either that it is present as colloidal particles smaller than 0.45 µm, the size of filter used, or that pH has been modified due to sampling problems (section 4.3). Iron and Mn are low in the superficial deposit groundwaters reflecting their oxidising nature.

5.4 **Rheidol groundwaters**

The summary data for the Rheidol groundwaters is shown in Tables 5.5 for major and minor solutes and Table 5.6 for trace elements. The groundwaters of the Rheidol have been sub-divided on the basis of lithology into superficial deposit groundwaters and bedrock +/- superficial deposit groundwaters. In the latter case, most boreholes are likely to be dominated by bedrock, but insufficient details were available to characterise them fully. The four superficial deposit groundwaters were from glaciofluvial gravels in the Rheidol Valley, and may not be representative of other types of superficial deposits in the catchment.

5.4.1 *Water types and physicochemical characteristics*

Groundwater temperatures vary from 10 to 17 °C (Table 5.5), but are typically 10 to 14 °C. The range in pH is relatively large, from moderately acidic (minimum pH 5.5) to slightly acidic (maximum pH 6.8). The SEC also varies from very fresh (44 µS cm⁻¹) to moderately mineralised (368 cm⁻¹). Redox measurements (Eh and DO) in the bedrock group groundwaters indicate that the groundwaters vary from oxidising to reducing (Eh from 2 to 368 mV). The superficial deposit groundwaters sampled were variable in terms of redox potential (Eh from 2 to 432 mV). Many of the sources were springs and the redox measurements are likely to have been affected by contact with the atmosphere, but the range in concentrations of redox sensitive parameters (N-species, Fe, Mn) indicates a large range in redox conditions.

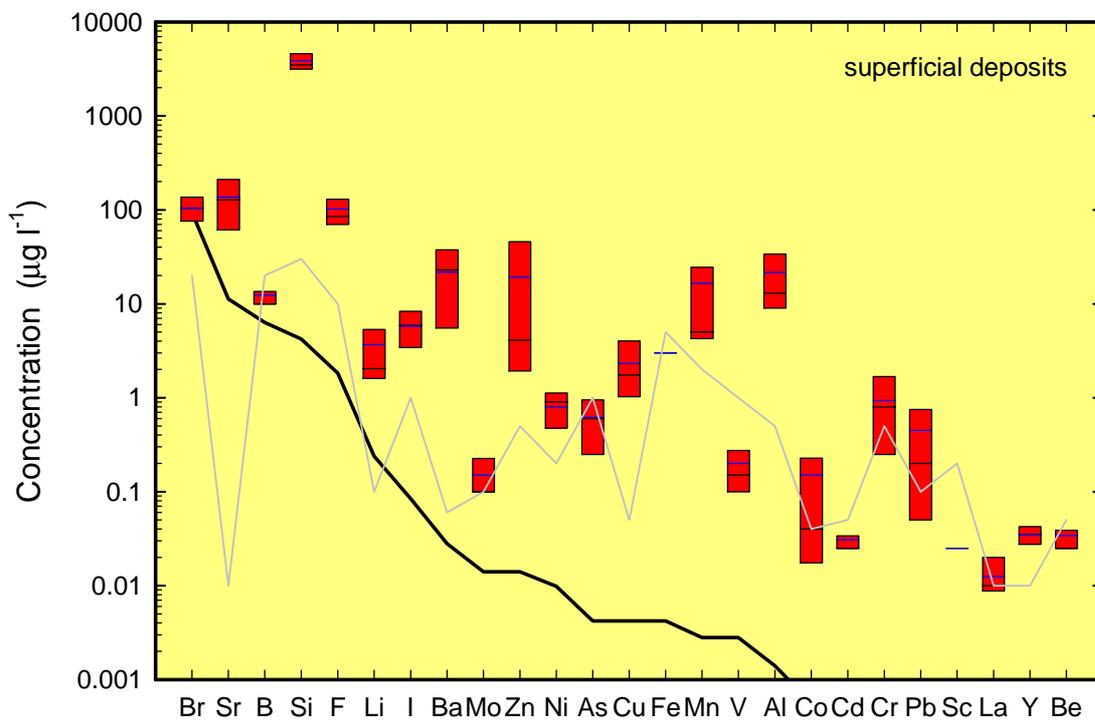
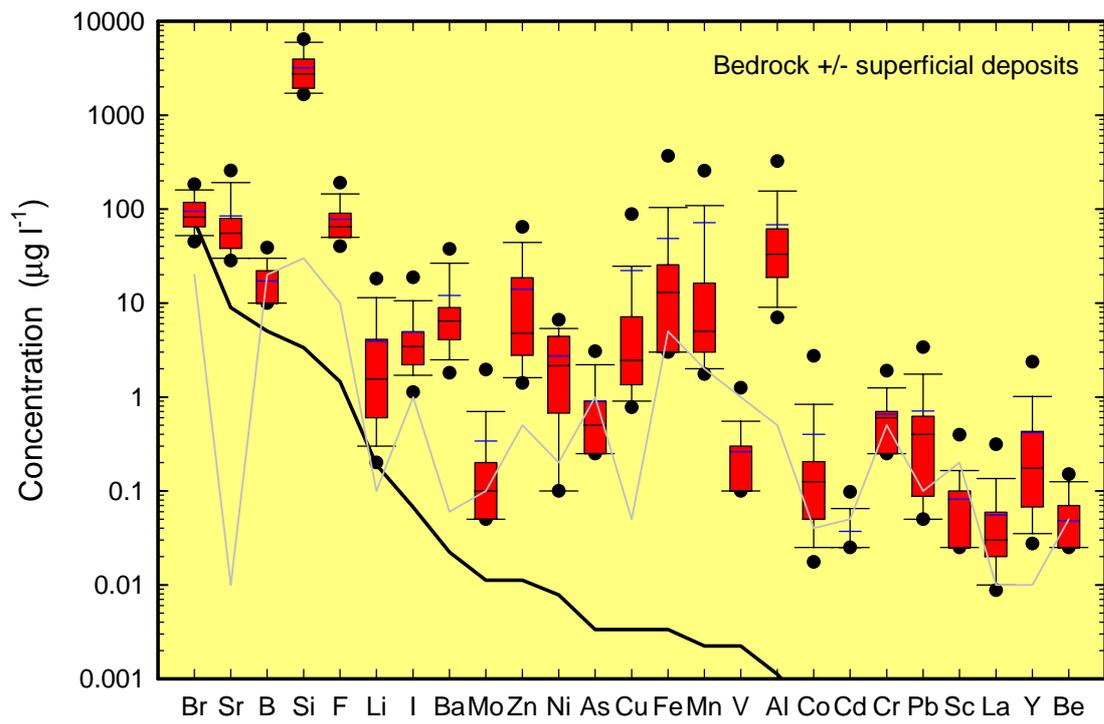


Figure 5.9 Boxplots for minor and trace elements in groundwaters of the Teifi catchment.

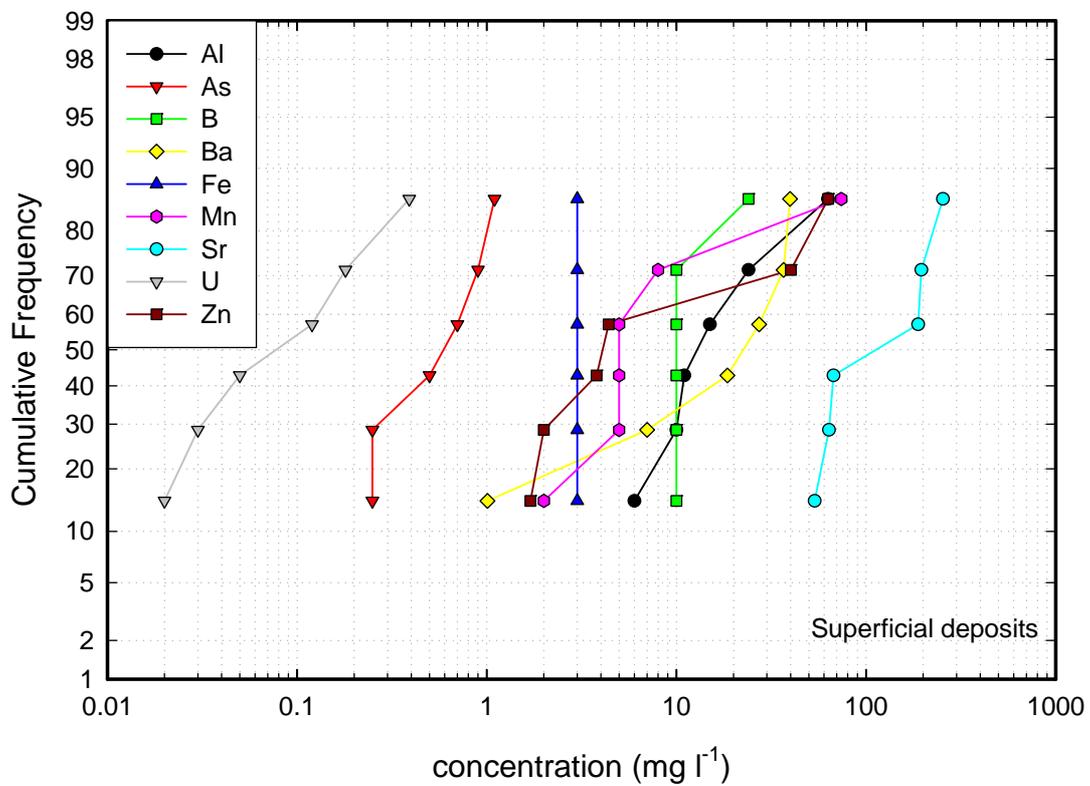
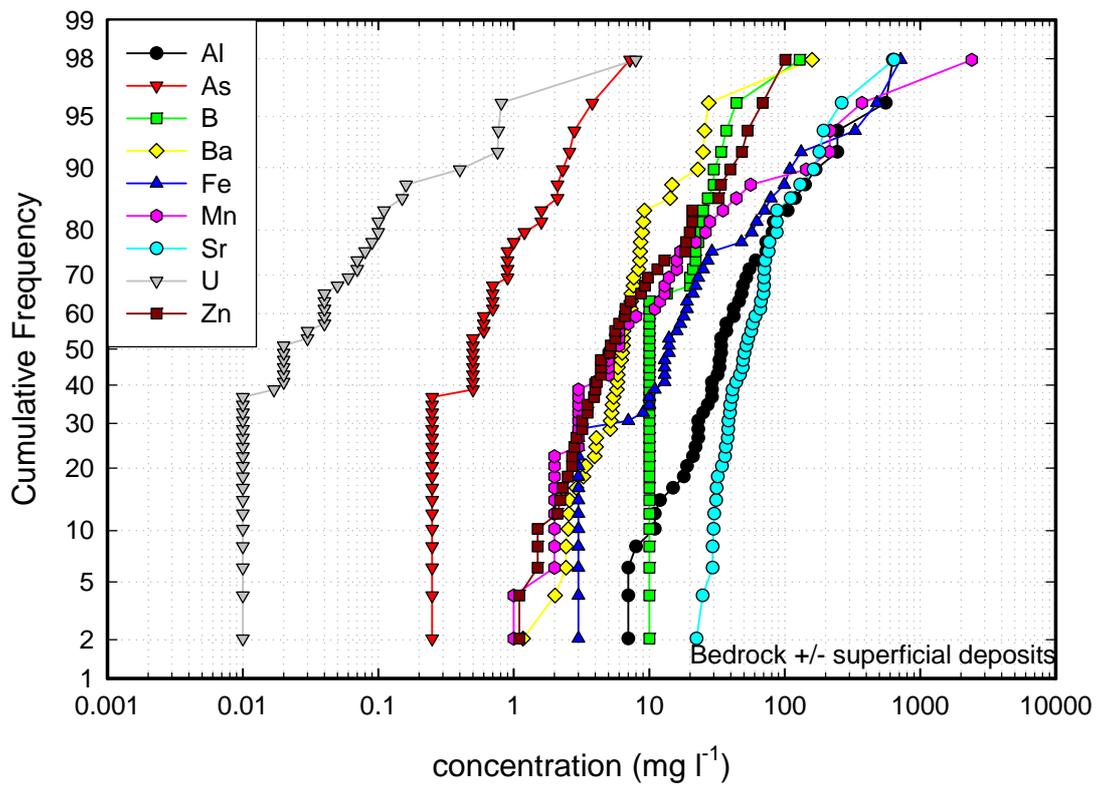


Figure 5.10 Cumulative probability plots for trace elements in groundwaters of the Teifi catchment.

Table 5.5 Major and minor element data for groundwaters in the Rheidol Valley.

	Units	Rheidol bedrock +/- superficial						Rheidol gravels					
		Min.	Max.	Median	Mean	97.7 th %	N	Min.	Max.	Median	Mean	97.7 th %	N
T	°C	10.2	16.6	11.9	13.3	16.3	15	10.5	11.7	11.3	11.2	11.7	4
pH		5.48	6.76	6.11	6.11	6.72	15	5.77	6.81	6.08	6.19	6.77	4
Eh	mV	60	368	139	185	359	15	2	139	127	99	139	4
DO	mg l ⁻¹	0.7	9.0	4.8	5.2	8.5	15	<0.1	3.4	3.2	2.5	3.4	4
SEC	µS cm ⁻¹	44	376	137	143	342	15	200	367	222	253	358	4
Ca	mg l ⁻¹	1.5	24.2	8.9	9.8	23.2	15	10.2	26.3	17.3	17.8	25.7	4
Mg	mg l ⁻¹	0.7	8.6	3.3	3.3	8.3	15	5.8	7.0	6.5	6.4	6.9	4
Na	mg l ⁻¹	3.8	27.7	8.5	9.6	23.7	15	11.7	38.9	13.1	19.2	37.1	4
K	mg l ⁻¹	<0.5	10.5	0.8	1.4	7.9	15	1.0	9.0	1.7	3.3	8.5	4
Cl	mg l ⁻¹	6.2	47.6	13.7	15.8	41.8	15	18.2	79.3	20.3	34.5	75.3	4
SO ₄	mg l ⁻¹	2.6	31.4	13.9	9.8	27.6	15	11.4	33.4	15.2	18.8	32.2	4
HCO ₃	mg l ⁻¹	5	51	21	21.3	48.4	15	21	66	35	39.3	63.9	4
NO ₃ -N	mg l ⁻¹	<0.1	11.8	0.7	2.6	11.1	15	0.2	10.5	4.0	4.7	10.3	4
NO ₂ -N	µg l ⁻¹	1	10	2	3	8	15	1	6	2	3	6	4
NH ₄ -N	µg l ⁻¹	<3	193	10	33	189	15	<3	134	<3	35	125	4
P	µg l ⁻¹	<20	40	22	21	38	15	<20	74	40	41	72	4
DOC	mg l ⁻¹	0.8	11.3	2.5	3.6	9.9	15	1.1	2.6	1.9	1.8	2.5	4
F	mg l ⁻¹	<0.1	<0.1	<0.1	<0.1	<0.1	15	<0.1	<0.1	<0.1	<0.1	<0.1	4
Br	µg l ⁻¹	<30	102	57	52	95	15	58	64	61	61	64	4
I	µg l ⁻¹	<1	7	2	3	6	15	<1	14	2	5	13	4
Si	mg l ⁻¹	1.5	4.0	2.9	2.6	3.9	15	2.8	6.1	4.4	4.4	6.0	4

Table 5.6 Trace element data for groundwaters in the Rheidol Valley.

	Rheidol Valley bedrock +/-Superficial deposits						Superficial deposits						
	Minimum	Maximum	Median	Mean	97.7th %	N	Minimum	Maximum	Median	Mean	97.7th %	N	
Ag	µg l ⁻¹	<0.05	0.10	<0.05	<0.05	0.08	15	<0.05	<0.05	<0.05	<0.05	<0.05	4
Al	µg l ⁻¹	3	350	7	63	298	15	2	7	3	4	7	4
As	µg l ⁻¹	<0.05	0.7	<0.05	<0.05	0.7	15	<0.05	1.2	<0.05	<0.05	1.1	4
Au	µg l ⁻¹	0.03	0.03	0.03	0.03	0.03	15	0.03	0.03	0.03	0.03	0.03	4
B	µg l ⁻¹	<20	30	<20	<20	27	15	<20	22	<20	<20	21	4
Ba	µg l ⁻¹	0.4	11.4	3.1	3.8	11.0	15	0.8	4.4	2.7	2.7	4.3	4
Be	µg l ⁻¹	<0.05	0.18	<0.05	0.05	0.18	15	<0.05	<0.05	<0.05	<0.05	<0.05	4
Bi	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	15	<0.05	<0.05	<0.05	<0.05	<0.05	4
Cd	µg l ⁻¹	0.06	0.28	0.19	0.13	0.27	15	0.07	0.22	0.15	0.15	0.22	4
Ce	µg l ⁻¹	<0.01	0.29	0.03	0.06	0.26	15	<0.01	0.03	0.01	0.01	0.03	4
Co	µg l ⁻¹	0.03	1.36	0.30	0.36	1.35	15	0.06	2.24	0.11	0.63	2.10	4
Cr	µg l ⁻¹	<0.5	<0.5	<0.5	<0.5	<0.5	15	<0.5	<0.5	<0.5	<0.5	<0.5	4
Cs	µg l ⁻¹	<0.01	3.85	0.12	0.45	2.92	15	0.07	0.20	0.15	0.14	0.20	4
Cu	µg l ⁻¹	0.4	11.8	1.7	2.9	11.3	15	0.5	1.7	0.7	0.9	1.6	4
Dy	µg l ⁻¹	<0.01	0.14	0.02	0.05	0.14	15	<0.01	0.02	0.01	0.01	0.02	4
Er	µg l ⁻¹	<0.01	0.09	0.01	0.03	0.09	15	<0.01	0.01	<0.01	<0.01	0.01	4
Eu	µg l ⁻¹	<0.01	0.03	0.01	0.01	0.03	15	<0.01	0.01	<0.01	<0.01	0.01	4
Fe	mg l ⁻¹	<0.005	0.771	<0.005	0.107	0.643	15	<0.005	<0.005	<0.005	<0.005	<0.005	4
Ga	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	15	<0.05	0.12	<0.05	<0.05	0.11	4
Gd	µg l ⁻¹	<0.01	0.17	0.04	0.06	0.16	15	<0.01	0.04	0.02	0.02	0.04	4
Ge	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	15	<0.05	<0.05	<0.05	<0.05	<0.05	4
Hf	µg l ⁻¹	<0.02	<0.02	<0.02	<0.02	<0.02	15	<0.02	<0.02	<0.02	<0.02	<0.02	4
Hg	µg l ⁻¹	<0.1	<0.1	<0.1	<0.1	<0.1	15	<0.1	<0.1	<0.1	<0.1	<0.1	4
Ho	µg l ⁻¹	<0.01	0.03	<0.01	0.01	0.03	15	<0.01	<0.01	<0.01	<0.01	<0.01	4
In	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	15	<0.01	<0.01	<0.01	<0.01	<0.01	4
Ir	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	15	<0.05	<0.05	<0.05	<0.05	<0.05	4
La	µg l ⁻¹	<0.01	0.17	0.02	0.04	0.14	15	<0.01	0.02	0.02	0.01	0.02	4
Li	µg l ⁻¹	0.3	2.2	1.8	1.2	2.1	15	0.6	5.6	2.2	2.6	5.4	4
Lu	µg l ⁻¹	<0.01	0.01	<0.01	<0.01	0.01	15	<0.01	<0.01	<0.01	<0.01	<0.01	4
Mn	mg l ⁻¹	<0.002	0.168	0.025	0.032	0.140	15	0.004	6.810	0.558	1.983	6.417	4
Mo	µg l ⁻¹	<0.1	0.1	<0.1	<0.1	0.1	15	<0.1	0.3	0.2	0.2	0.3	4
Nb	µg l ⁻¹	<0.01	0.01	<0.01	<0.01	<0.01	15	<0.01	<0.01	<0.01	<0.01	<0.01	4
Nd	µg l ⁻¹	0.01	0.26	0.08	0.10	0.26	15	<0.01	0.09	0.04	0.04	0.09	4
Ni	µg l ⁻¹	<0.2	3.9	1.1	0.9	3.2	15	<0.2	1.4	0.7	0.7	1.4	4
Os	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	15	<0.05	<0.05	<0.05	<0.05	<0.05	4
Pb	µg l ⁻¹	<0.1	12.1	0.2	1.2	9.1	15	0.1	0.1	0.1	0.1	0.1	4
Pd	µg l ⁻¹	<0.2	<0.2	<0.2	<0.2	<0.2	15	<0.2	<0.2	<0.2	<0.2	<0.2	4
Pr	µg l ⁻¹	<0.01	0.05	0.01	0.02	0.05	15	<0.01	0.01	0.01	0.01	0.01	4
Pt	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	15	<0.01	<0.01	<0.01	<0.01	<0.01	4
Rb	µg l ⁻¹	0.1	11.7	0.9	1.8	9.0	15	0.9	4.9	1.9	2.4	4.7	4
Re	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	15	<0.01	<0.01	<0.01	<0.01	<0.01	4
Rh	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	15	<0.01	<0.01	<0.01	<0.01	<0.01	4
Ru	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	15	<0.05	<0.05	<0.05	<0.05	<0.05	4
Sb	µg l ⁻¹	<0.05	0.51	<0.05	0.09	0.46	15	<0.05	<0.05	<0.05	<0.05	<0.05	4
Sc	µg l ⁻¹	<1	1	1	1	1	15	<1	1	1	1	1	4
Se	µg l ⁻¹	<0.5	0.7	<0.5	<0.5	0.7	15	<0.5	0.6	0.5	<0.5	0.6	4
Sm	µg l ⁻¹	<0.02	0.11	0.03	0.04	0.10	15	<0.02	0.03	0.02	0.02	0.03	4
Sn	µg l ⁻¹	0.06	0.14	0.11	0.11	0.14	15	0.10	0.18	0.13	0.13	0.18	4
Sr	µg l ⁻¹	11	74	25	31	73	15	43	67	53	54	67	4
Ta	µg l ⁻¹	<0.02	<0.02	<0.02	<0.02	<0.02	15	<0.02	<0.02	<0.02	<0.02	<0.02	4
Tb	µg l ⁻¹	<0.01	0.02	<0.01	<0.01	0.02	15	<0.01	<0.01	<0.01	<0.01	<0.01	4
Te	µg l ⁻¹	< .05	< .05	< .05	< .05	< .05	15	< .05	< .05	< .05	< .05	< .05	4
Th	µg l ⁻¹	< .05	< .05	< .05	< .05	< .05	15	< .05	< .05	< .05	< .05	< .05	4
Ti	µg l ⁻¹	<10	<10	<10	<10	<10	15	<10	<10	<10	<10	<10	4
Tl	µg l ⁻¹	<0.01	0.01	<0.01	<0.01	0.01	15	<0.01	0.01	<0.01	<0.01	<0.01	4
Tm	µg l ⁻¹	<0.01	0.01	<0.01	<0.01	0.01	15	<0.01	<0.01	<0.01	<0.01	<0.01	4
U	µg l ⁻¹	<0.02	0.08	<0.02	0.02	0.08	15	<0.02	0.07	<0.02	0.03	0.07	4
V	µg l ⁻¹	<0.2	0.4	0.2	0.2	0.4	15	<0.2	0.3	<0.2	<0.2	0.3	4
W	µg l ⁻¹	<0.02	0.03	<0.02	<0.02	0.03	15	<0.02	0.02	0.02	<0.02	0.02	4
Y	µg l ⁻¹	0.02	1.06	0.15	0.28	1.05	15	0.01	0.15	0.09	0.08	0.15	4
Yb	µg l ⁻¹	<0.01	0.08	0.01	0.02	0.08	15	<0.01	0.01	<0.01	<0.01	0.01	4
Zn	µg l ⁻¹	6	210	24	46	188	15	11	68	21	31	65	4
Zr	µg l ⁻¹	<0.02	0.08	<0.02	0.02	0.08	15	<0.02	<0.02	<0.02	<0.02	<0.02	4

On a Piper plot (Figure 5.11), the groundwaters vary from Ca-HCO₃ type to mixed cation-Cl types, similar to those found in the Plynlimon and Teifi catchments. The groundwaters from the two groups show significant overlap, but groundwaters within the superficial deposits group tend to be less enriched in HCO₃ relative to Cl (opposite to those in the Teifi Valley, Figure 5.6). For the bedrock groundwaters, there is a tendency for the lower TDS and more acidic groundwaters to be dominated by Na-Cl-SO₄ types. The two surface water samples are shown for comparison. The River Rheidol sample sits in the field of the groundwaters, but has lower SEC. The second sample, a small tributary, contained much higher relative SO₄ (SO₄ of 31 mg l⁻¹). This stream water also contained enhanced concentrations of Cd (8 µg l⁻¹), Cu (27 µg l⁻¹), Ni (20 µg l⁻¹), Pb (13 µg l⁻¹) and Zn (3702 µg l⁻¹) and it

is likely that there is some contamination from either mineralised bedrock or from previous mining activities. Concentrations of these metals in a spring sample collected adjacent to the stream were not high, being similar to other springs sampled.

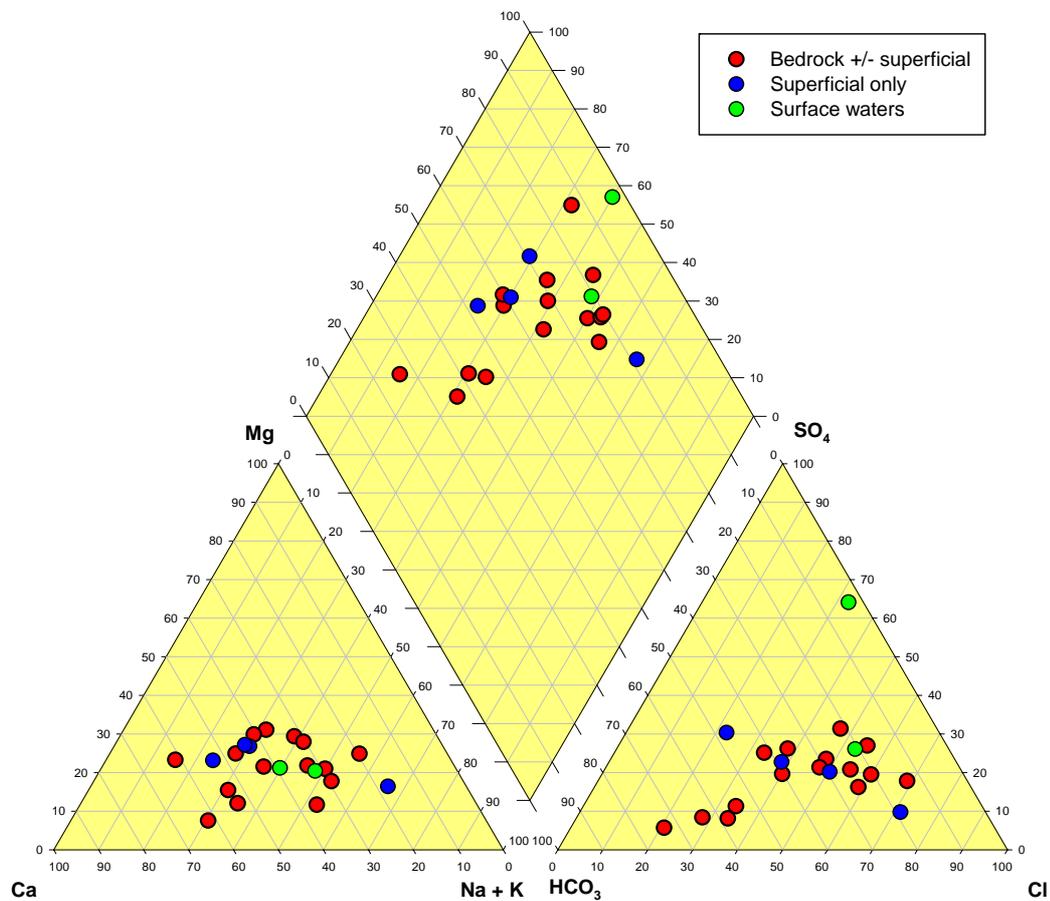


Figure 5.11 PIPER plot showing the relative proportions of major elements in the Rheidol Valley groundwaters.

5.4.2 Major elements

Median concentrations of major elements were slightly higher in groundwaters in the superficial gravel deposits, but the number of samples was small ($n=4$) and probably not representative of other superficial deposit groundwaters. Maximum concentrations of Na, Cl and Si were significantly above those of the bedrock group. Nevertheless, there are no clear differences in the ranges of major solutes as shown on the boxplots and cumulative probability plots (Figures 5.12 and 5.13).

Bicarbonate and Cl form the dominant anions, and Na and Ca the dominant cations, in most waters (Figures 5.12 and 5.13). Most elements show trends approaching log-normal, but NO_3 shows a long tail at low concentrations. Many samples contained low K, and many were below the limit of detection (0.5 mg l^{-1}). The groundwater with high K also contained high Cl, SO_4 and NO_3 , and the high K is, therefore, likely to be of anthropogenic origin.

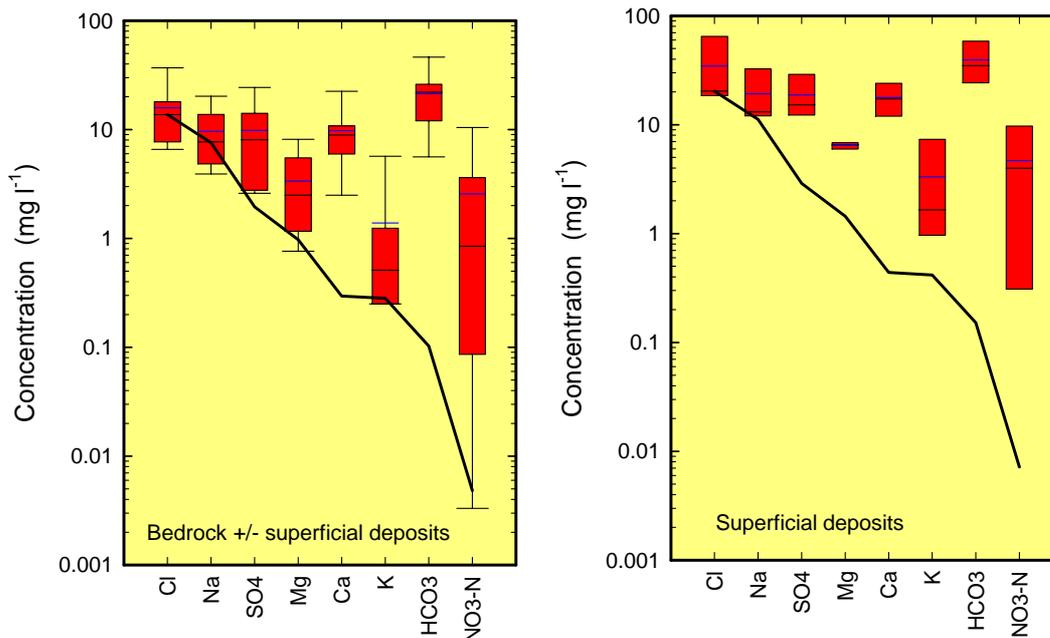


Figure 5.12 Boxplots for major and minor elements in groundwaters of the Rheidol catchment.

5.4.3 Minor and trace elements

Trace elements data are shown on Table 5.6 and displayed on boxplots and cumulative probability plots on Figures 5.14 and 5.15 respectively. The concentrations of most trace elements are generally very low. Aluminium varies from 3 to 350 $\mu\text{g l}^{-1}$ in the bedrock groundwaters but is less than 7 $\mu\text{g l}^{-1}$ in the gravel groundwaters. Zinc may be locally enhanced, up to 210 $\mu\text{g l}^{-1}$. A correlation of Zn with Cd and Ni points towards bedrock sulphide mineralisation as the dominant source. Iron concentrations in the bedrock up to 770 $\mu\text{g l}^{-1}$ occur, but Fe is typically very low with median concentrations in both groups below the limit of detection (5 $\mu\text{g l}^{-1}$). Manganese is generally much higher in the gravel groundwaters reaching 6810 $\mu\text{g l}^{-1}$ in the Ty Llwyd borehole. Concentrations in groundwaters of the Trering boreholes vary widely from 3.9 to 1110 $\mu\text{g l}^{-1}$. The high Mn is associated with very low NO_3 implying a redox control; the low Mn samples have very high NO_3 consistent with oxidising conditions

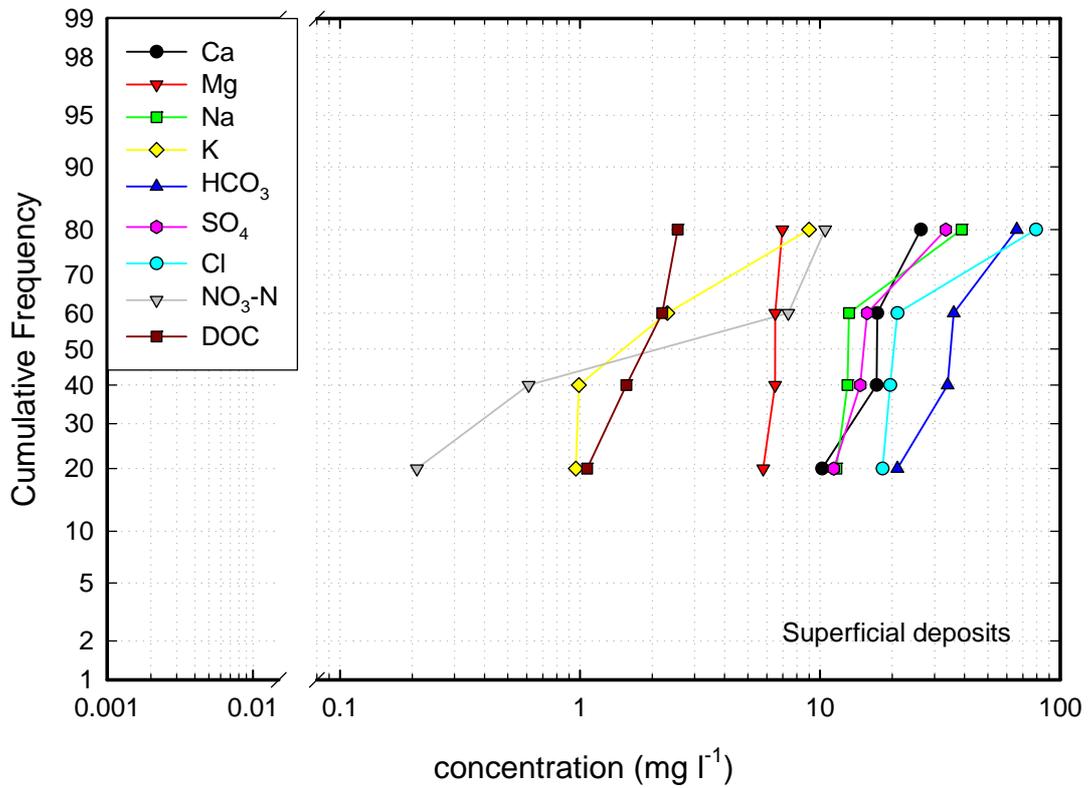
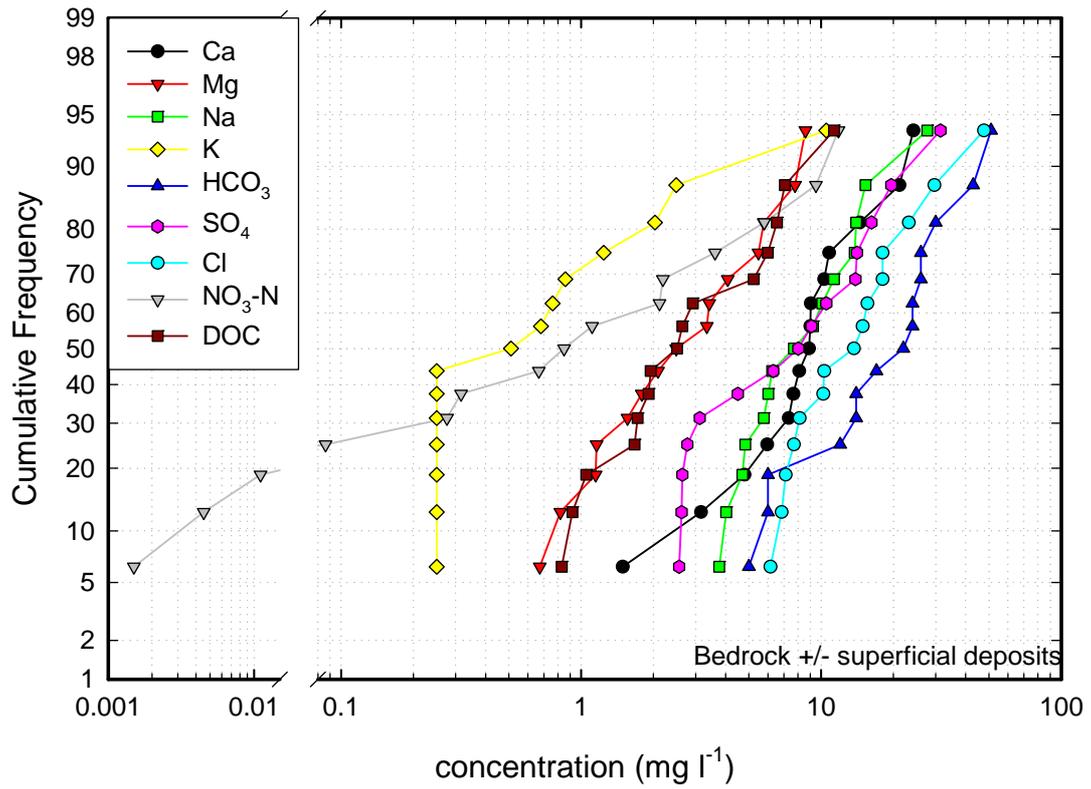


Figure 5.13 Cumulative probability plots for major and minor elements in groundwaters of the Rheidol catchment.

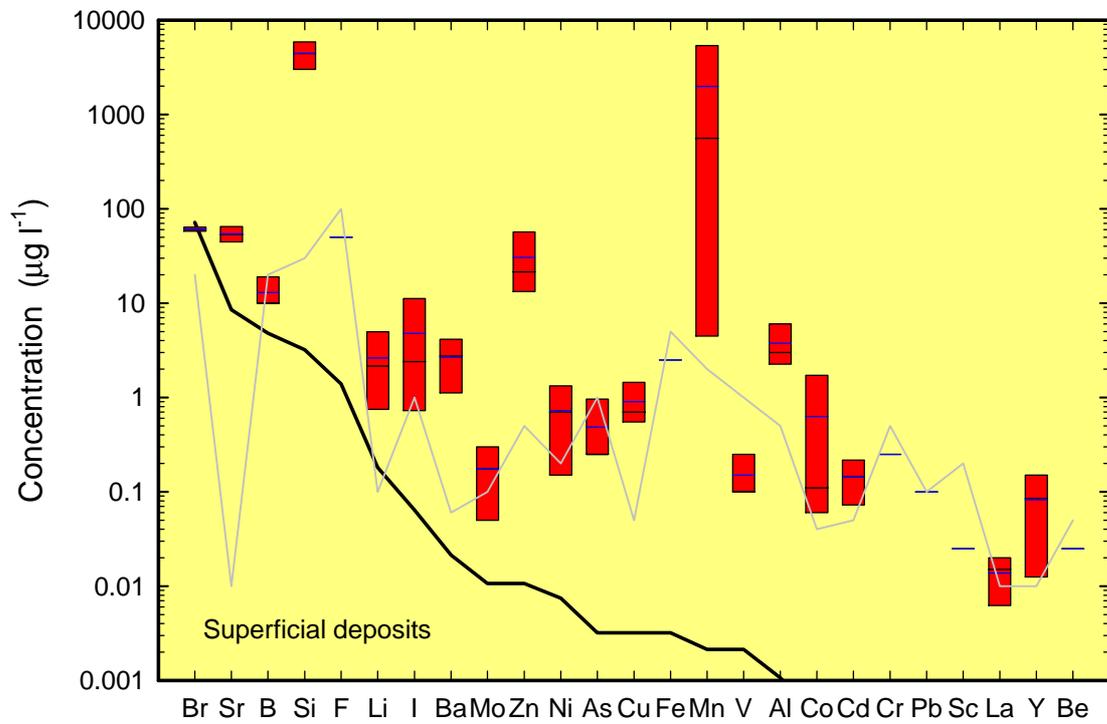
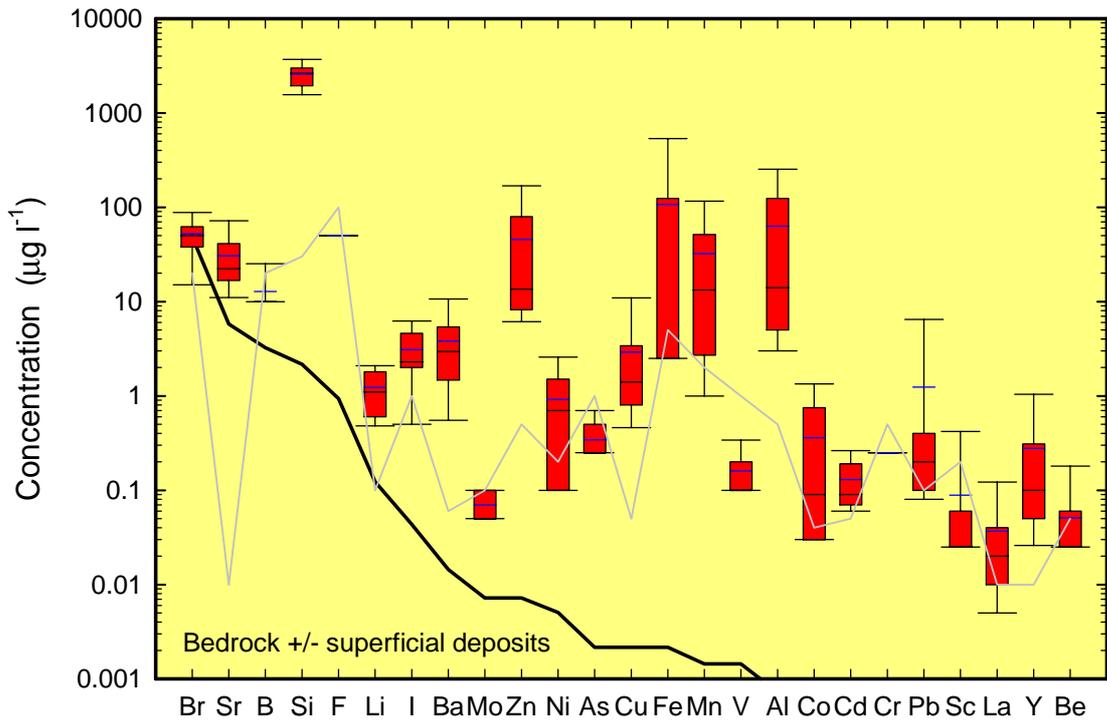


Figure 5.14 Boxplots for minor and trace elements in groundwaters of the Rheidol catchment.

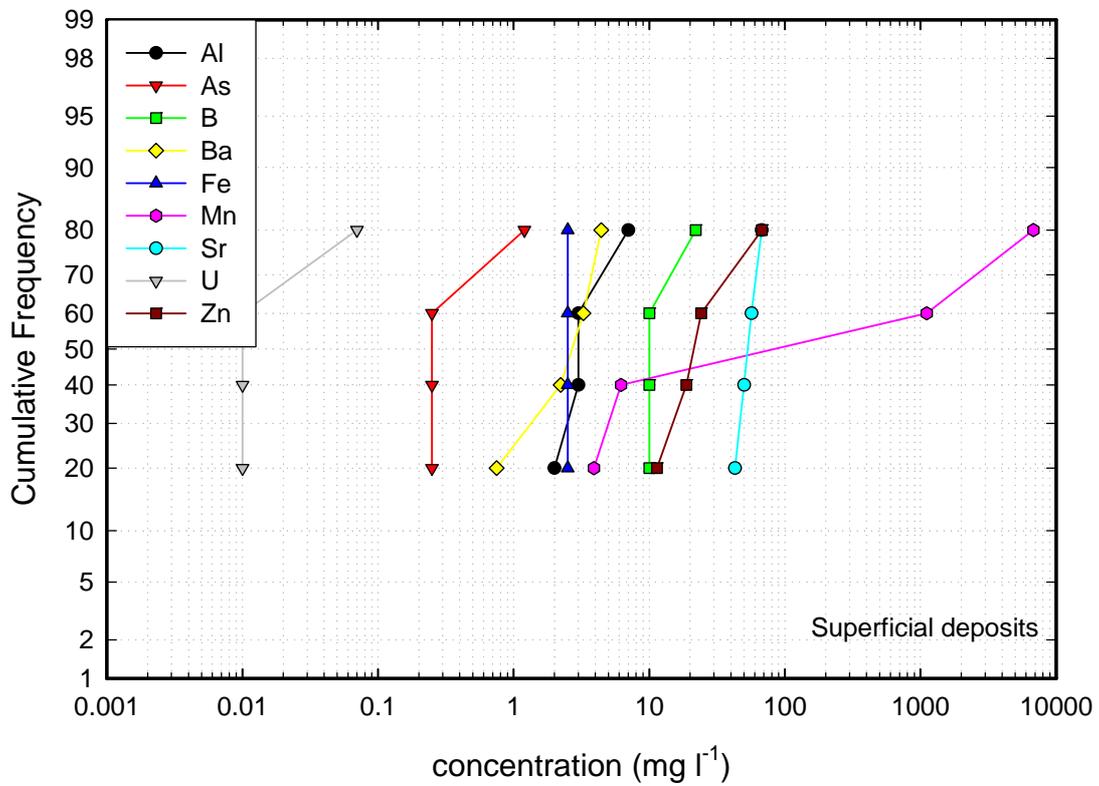
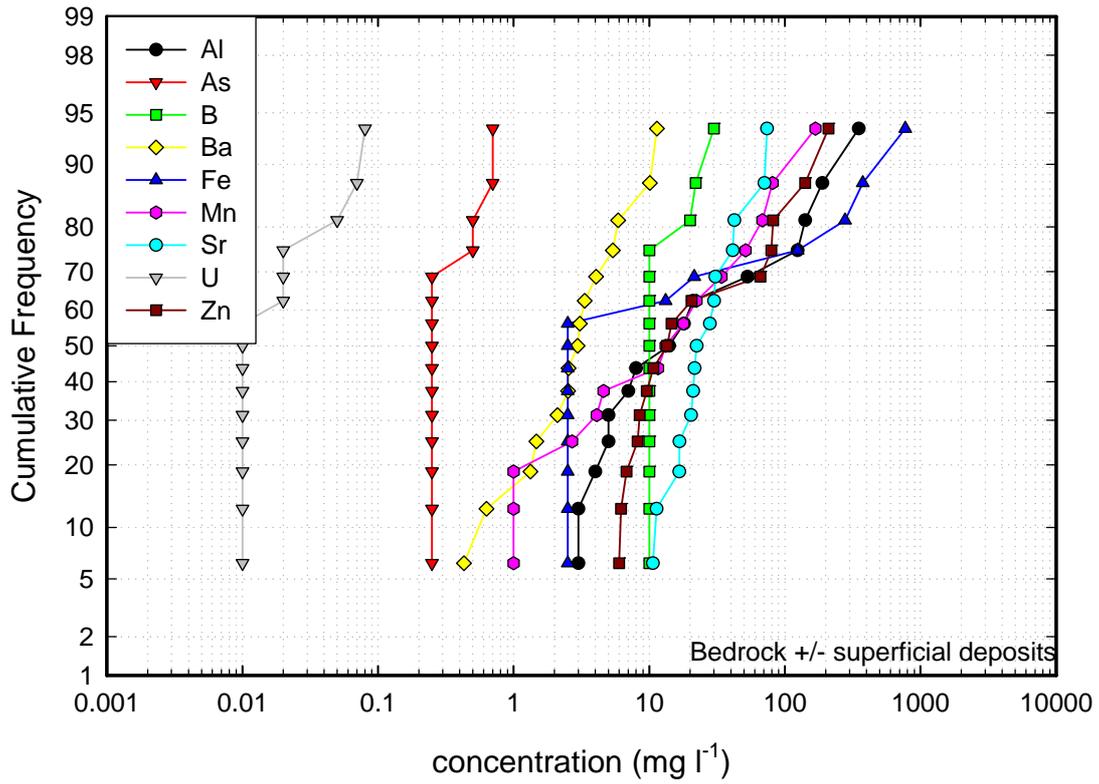


Figure 5.15 Cumulative probability plots for trace elements in groundwaters of the Rheidol catchment.

5.5 Pollution indicators

In order to determine baseline concentrations, it is desirable to study only pristine waters and avoid polluted waters since these may alter baseline concentrations either directly by adding solutes or indirectly by promoting chemical reactions in the aquifer (see Box 5.2).

It is generally difficult to obtain pristine waters, in part because waters may be sampled over a large screened interval where polluted waters are present at shallow depth or because diffuse pollution (especially agricultural pollution) is present in large parts of the shallow aquifer. Boreholes affected by point source pollution have been avoided but most groundwaters in unconfined aquifers do show the effects of agricultural pollution due to the application of fertilisers or pesticides over the past decades, indicated by high nitrate concentrations and the presence of pesticides (Box 5.2).

Many of the regions studied are upland areas where point source pollutants are unlikely. However, the effects of upland farming, forestry, acid rain and former mining activities are likely to have impacted on groundwater chemistry. These changes are not likely to have modified the median to any significant degree, but locally enhanced concentrations of dissolved components such as NO_3 and K indicate that the higher concentrations of some elements do not represent baseline. Slightly elevated Al concentrations in forested areas are also likely to be due to acidification of soils and subsequent mobilisation of Al.

Box 5.2 How can we distinguish pristine waters from polluted groundwater?

Groundwater prior to the industrial era (before c. 1800) emerged as springs or was taken from shallow wells, whilst the deeper reserves were in a pristine condition. The water first encountered using modern drilling practices would have had compositions reflecting true baseline determined only by geological and geochemical processes. Only rarely is it possible to find such waters because the majority of groundwaters sampled in the present study are derived from aquifers which have been developed for decades. The challenge in baseline is to recognise the impact of any human activities over and above the natural baseline in the data sets used.

The approach adopted is threefold:

- (i) to have evidence of groundwater age
- (ii) to extrapolate data series back to an initial time
- (iii) to use indicator elements in the groundwater, known to result from human activities. The most probable indicators of human activities are enhanced TOC and N species – especially NO_3 – the presence of substances such as agro-chemicals or industrial chemicals. The sets of data are examined for these substances as a clue to the presence of “contamination”, although it is difficult to quantify this. Even where traces of contamination are present, this may have little impact on the overall chemistry of the groundwater.

6. GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS

6.1 Introduction

The hydrochemistry of the groundwaters in the study catchments is controlled both by natural inputs (baseline) and inputs derived from anthropogenic sources. The initial input of solutes to aquifers is from rainfall which is generally very dilute and acidic (Table 3.4). Infiltration through soils generally increases this rainfall-derived acidity due to an increase in carbonic acid derived from root respiration and organic matter decomposition. The chemistry of recharge water as it passes through the unsaturated zone is generally controlled by the presence of soluble minerals particularly carbonates such as calcite or dolomite. The unsaturated zone of the Ordovician and Silurian bedrock is typically devoid of carbonate mineral phases and the consequent lack of buffering of acidity means that trace metal species can be mobilised more readily and enter into the groundwater. Further reaction takes place as the groundwater moves along fractures and gives rise to a wide range of chemistries depending on the minerals forming the aquifer matrix. This chapter aims to characterise the dominant processes controlling water chemistry in the groundwaters and to characterise regional variations

6.2 Plynlimon groundwaters

The Plynlimon samples were collected from a relatively small area (Figure 3.1), but highlight the differences between different land-use and the large depth variations in chemistry within the shallow bedrock. Several of the groundwater samples in the Severn catchment are from boreholes which are only cased to shallow depth, hence mixing is likely to occur in the borehole column. All of the Wye boreholes are screened to a few metres above the base of the borehole.

6.2.1 Depth variations in hydrochemistry

The groundwater chemistry in both the Wye and Severn catchment displays considerable variations with depth (Figures 6.1 – 6.3). The shallow groundwaters tend to be lower in TDS and more acidic and oxidising (Figure 6.1). Selected major elements and Si are shown on Figure 6.2. Calcium and HCO_3 are uniformly low at depths <5 m, but are more variable and usually higher at greater depths. The low Ca waters in the Severn catchment around 25-30 m have undergone ion-exchange, hence the lower Ca in these boreholes. Chloride shows little variation with depth, but tends to be higher in the forested Severn catchment groundwaters, probably as a result of afforestation. Silicon concentrations are low in the shallow bedrock groundwater but increase with depth, being slightly higher in the Wye than the Severn groundwaters at depths below about 3 m.

Selected minor and trace elements are displayed on Figure 6.3. Nitrate concentrations are generally low reaching a maximum concentration of 1.9 mg l^{-1} in the shallow oxidising groundwaters (Figure 6.3). At depth, where conditions are reducing, concentrations are typically close to or below detection limit. Manganese (as well as Fe) is high in many of the shallow groundwaters, particularly in the Wye catchment. This may be due to reducing conditions caused by more extensive drift deposits in this part of the Wye catchment. Aluminium is high in the shallow acidic groundwaters of both catchments. Many trace elements which typically increase with residence time are higher in the deeper waters (Figure 6.3).

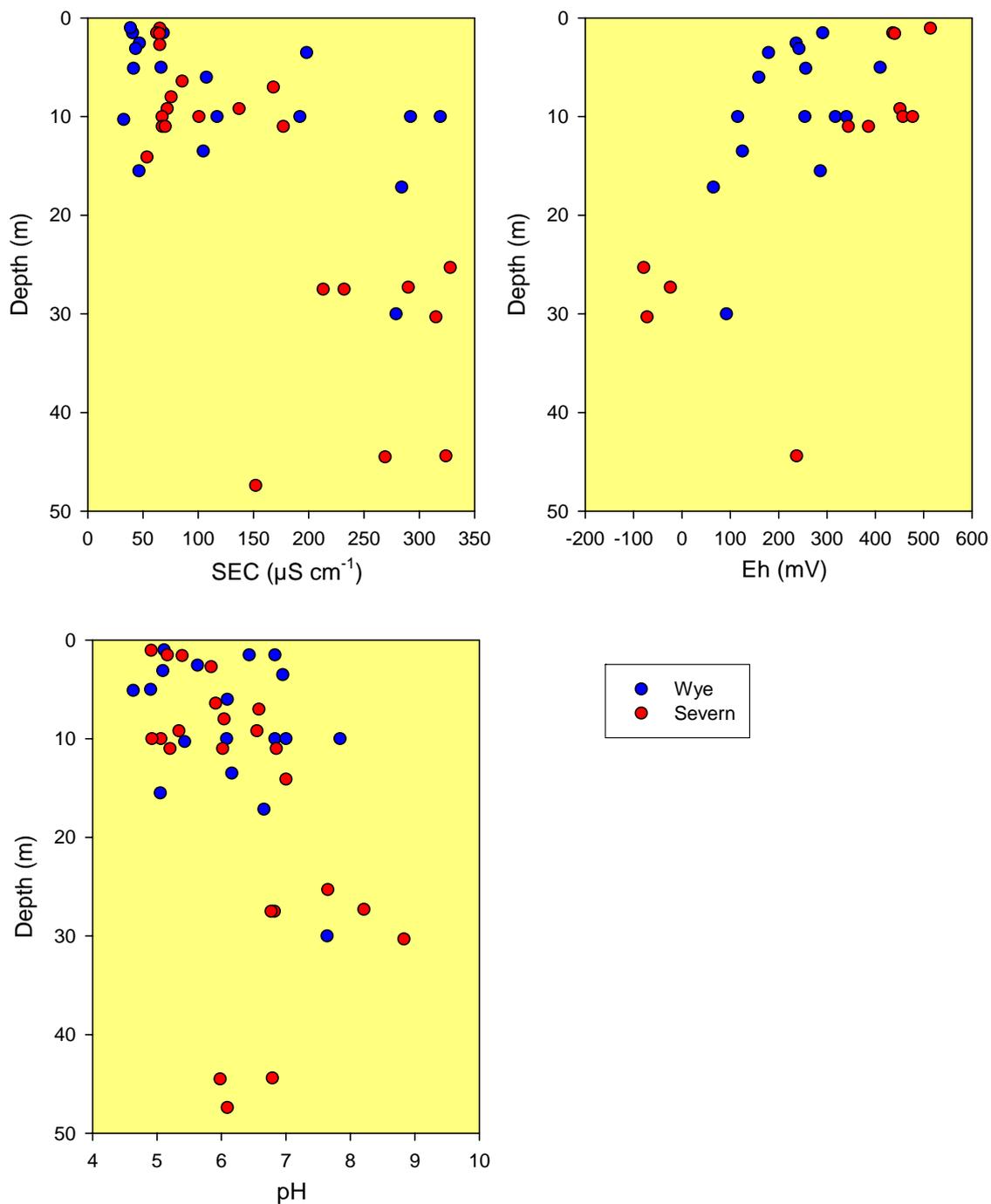


Figure 6.1 Specific Electrical Conductance, Eh and pH plotted against depth of borehole in the Plynlimon groundwaters.

6.2.2 Spatial variations in hydrochemistry

Spatial variations for selected solutes are shown on Figure 6.4. For most dissolved components, apart from Cl, there are no clear regional variations. The concentrations of Cl are higher in the forested Severn catchment. This difference has also been noted in the surface waters of the catchments (Shand et al., 1999b, 2005), being due to the increased evapotranspiration and the scavenging effect of

coniferous trees on atmospheric inputs. The other elements shown on Figure 6.4 (Ca, NO₃, Al) show the large variations present locally, a consequence of the different depths of boreholes in this highly stratified aquifer.

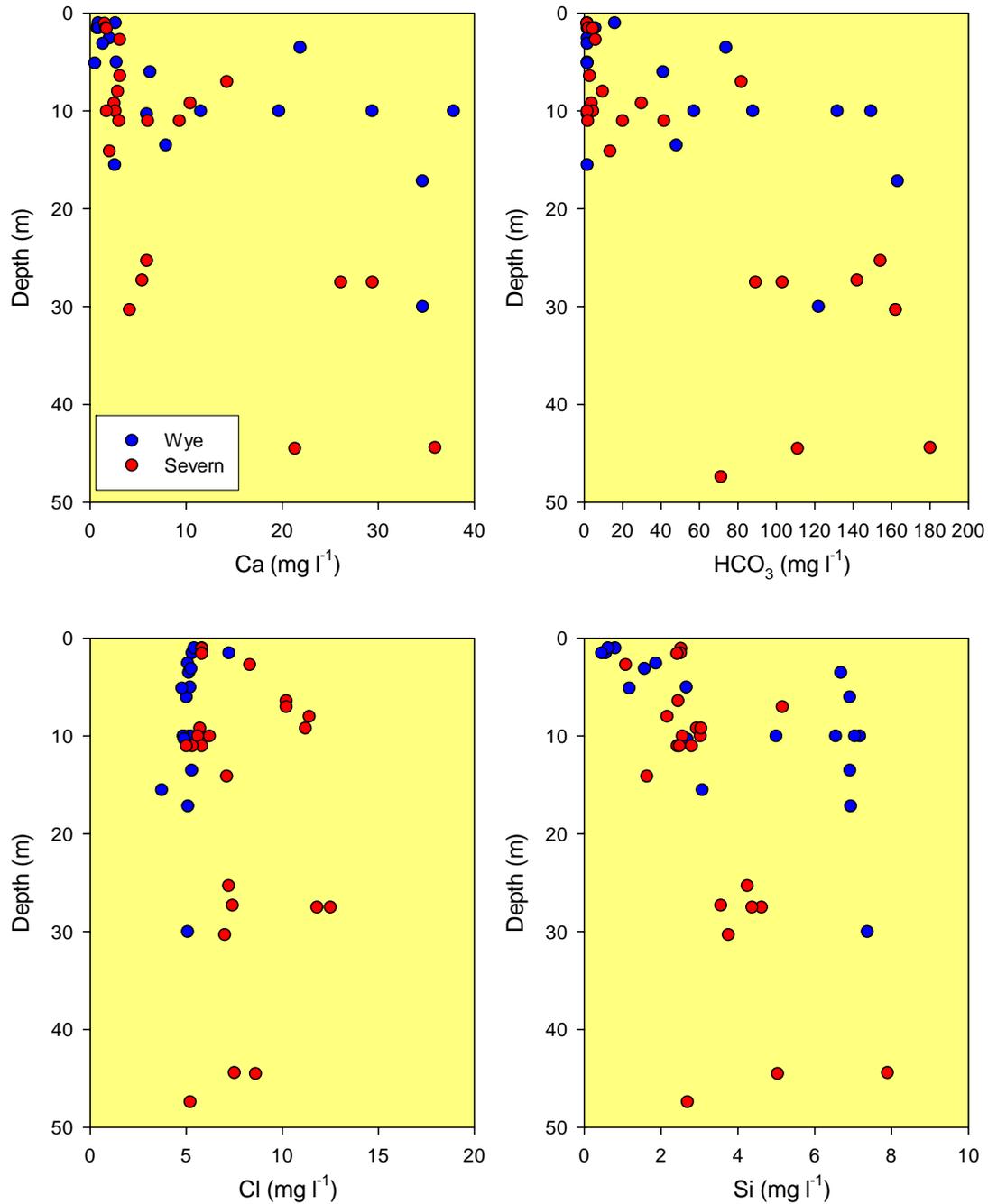


Figure 6.2 Selected major elements and Si plotted against depth of borehole for the Plynlimon groundwaters.

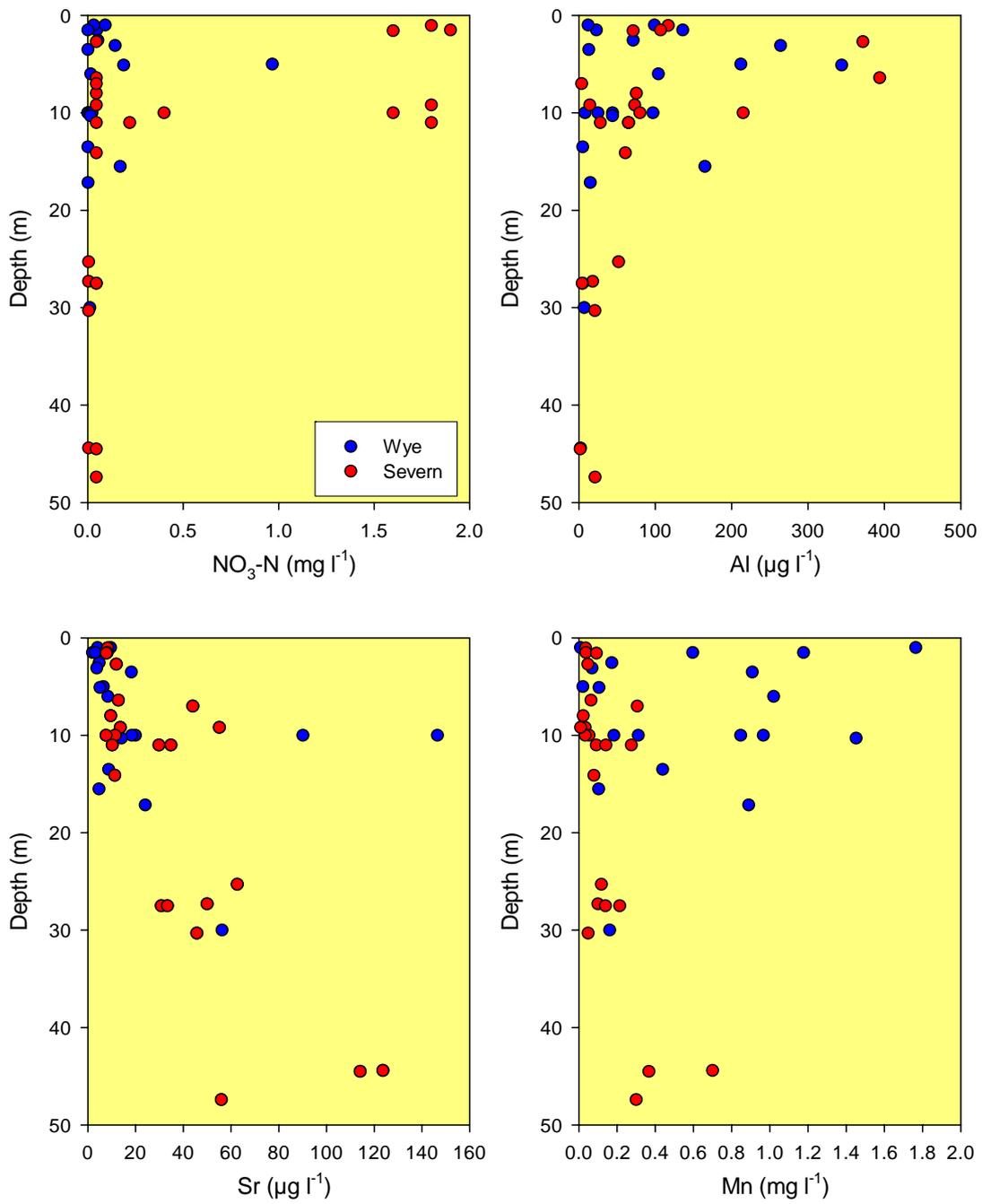


Figure 6.3 Nitrate and selected trace elements plotted against depth for the Plynlimon groundwaters.

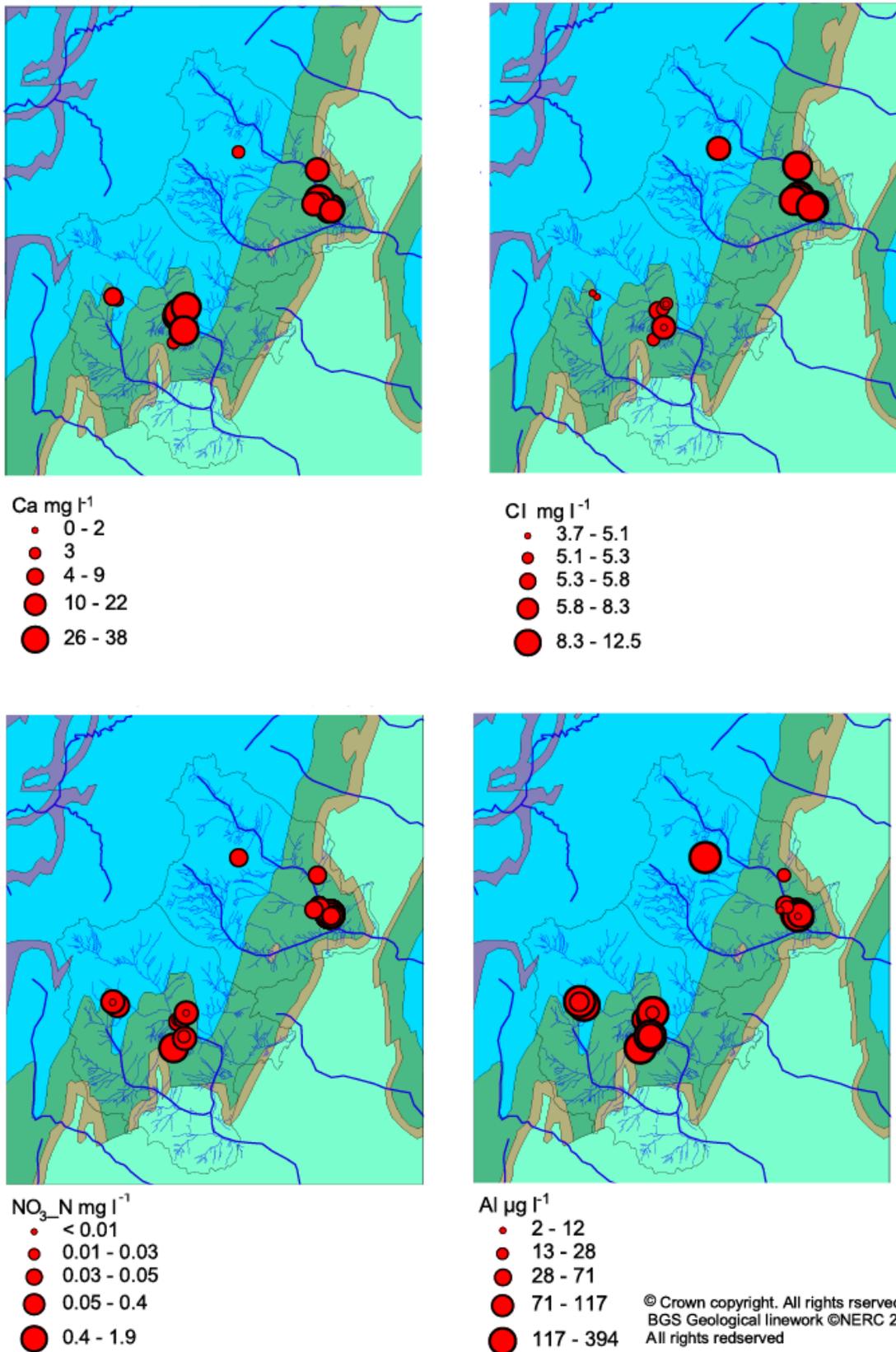


Figure 6.4 Spatial variations in concentrations of Ca, Cl, NO₃-N and Al in the Plynlimon groundwaters.

6.2.3 Mineral dissolution reactions

The relatively low SEC and concentrations of many solutes reflect the unreactive nature of the bedrock mineralogy. The Plynlimon catchments are susceptible to acidification due to the presence of acidic soils and slow mineral weathering rates. The dominant minerals in the mudstones and shales are an iron magnesium chlorite, a dioctahedral mica (sericite/illite) and quartz with lesser amounts of iron oxide, all of which weather slowly. A comparison of major elements with Cl shows that a significant proportion of the Na, and to a lesser degree Mg, is derived mainly from rainfall. The source of the water-rock-derived Mg and Fe is likely to be dominantly from the dissolution of chlorite. Magnesium is highest in the deeper groundwaters indicating that much of the weathering takes place in the aquifer, rather than in the acidic soils. The general correlation between Mg and Si (Figure 6.5) also indicates a dominant evolution by silicate dissolution.

The main source of K is likely to be from dissolution of K-feldspar or possibly illite, but the kinetics of dissolution of illite are likely to be slow. The origin of Ca is more problematic. Calcite occurs as a gangue mineral in the Pb-Zn veins which are present locally in parts of the catchment, but rare over the majority of the catchment. Shand et al. (1999a, 2001) argued, on the basis of Sr isotope data, that Ca-bearing feldspar is the most likely source of Ca because the isotope ratios of calcite were much lower than found in the groundwater. In addition, the Sr isotope ratios in the acidic soils (where no carbonate is present) were similar to those in the ground waters. Silicate dissolution is also indicated by the general correlation of Ca with Si (Figure 6.5). This is confirmed by the very negative isotope ratios of $\delta^{13}\text{C}$ with median value of -21 (Table 5.1) which indicate derivation of the C in HCO_3^- from soil-derived CO_2 and not carbonate minerals.

6.2.4 Redox reactions

Oxidation-reduction reactions play an important role in determining the stability and mobility of many chemical species, particularly N-species, S-species and trace elements which have different valencies. The redox status of the groundwaters varies from reducing to oxidising. In general oxidising conditions are prevalent in recharge areas and in groundwaters of shallow fractures.

Nitrate concentrations are highest in the more oxidising groundwaters (Figure 6.6). However, it should be noted that nitrate concentrations were found to increase after tree felling in the Plynlimon catchment (Neal et al., 2003), indicating the effects of land-use change in such relatively pristine areas. Nitrite and ammonium concentrations were often high in shallow groundwaters of the Wye catchment due to organic-rich soils or confinement beneath clay-rich drift deposits. A strong smell of H_2S was noted in several boreholes, indicating that sulphate-reducing conditions occur at depth, and in shallow ground waters beneath organic-rich soils and clay. Sulphate concentrations are variable and although concentrations are low (up to 24 mg l^{-1}), the maximum concentrations are much higher than due to rainfall inputs. The dominant source is likely to be from oxidation of sulphide minerals particularly the Gwestyn shales.

Iron and Mn were locally high, showing an antithetic relationship with NO_3^- as expected from their increased solubility under reducing conditions (Figure 6.6). Arsenic is generally more mobile under reducing conditions and concentrations were highest in the more reducing groundwaters (Figure 6.7).

6.2.5 Ion exchange reactions

Ion-exchange reactions are not considered to be a dominant process in the groundwaters of the Plynlimon catchment. However, three boreholes at one locality on the lower slopes of the Hafren catchment were of Na- HCO_3^- type (Figure 5.1). These groundwaters contained low Ca concentrations in comparison with other groundwaters in the catchment and had very high (8-9) Na/Cl ratios. It is likely that these have undergone ion-exchange of dissolved Ca for exchangeable Na on clays.

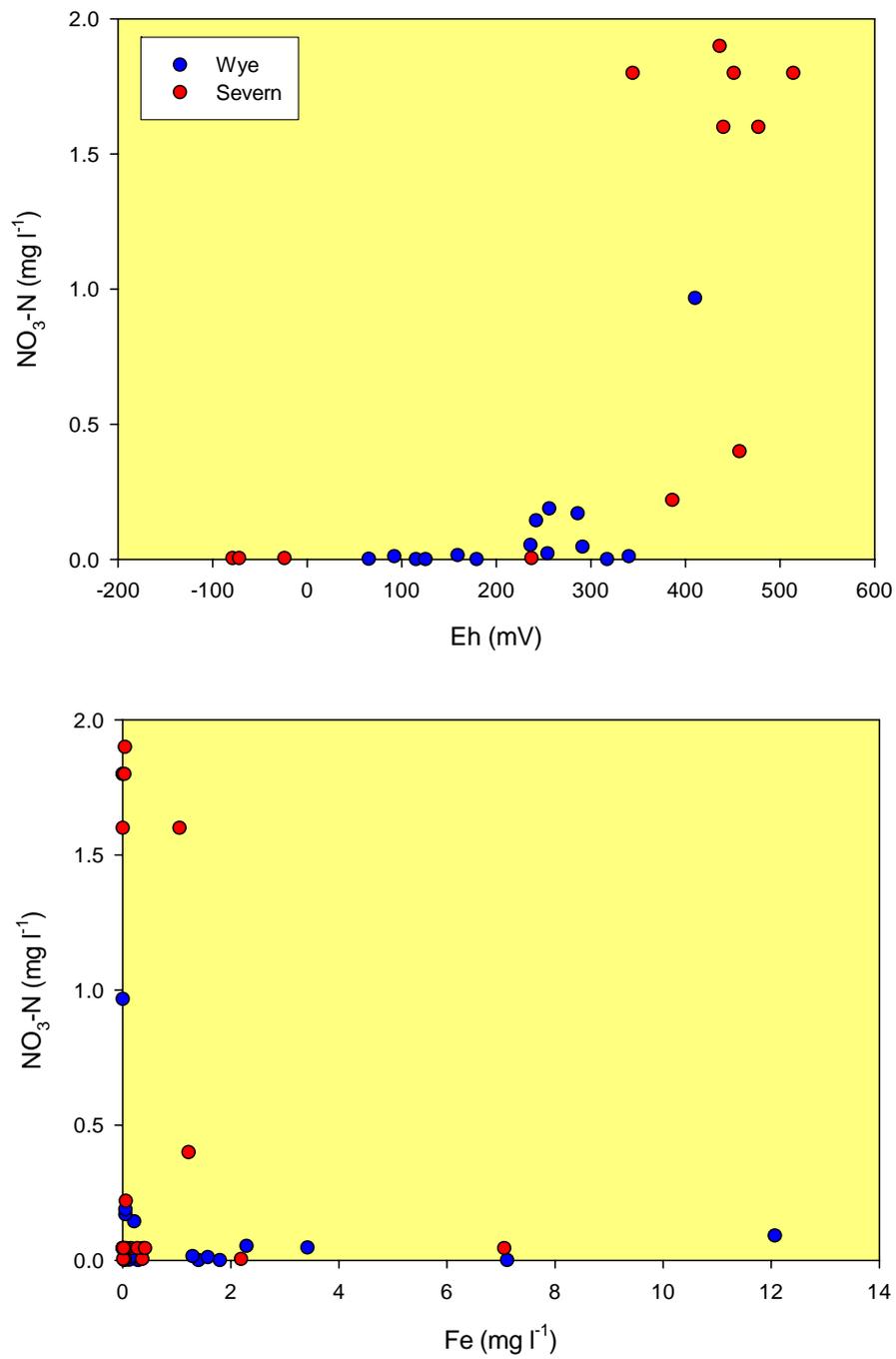


Figure 6.6 Plots of Eh and Fe vs. nitrate for the Plynlimon groundwaters.

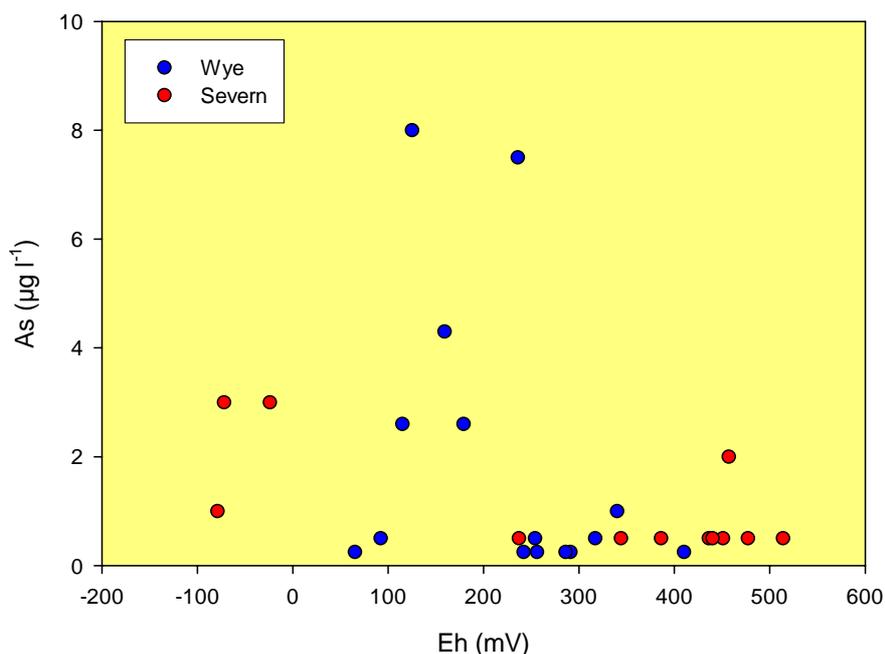


Figure 6.7 Arsenic concentrations plotted against Eh for the Plylimon groundwaters.

6.2.6 *Mixing with older formation water*

The low Cl concentrations in all groundwaters (maximum of 12.5 mg l⁻¹) are consistent with bulk rainfall inputs modified by evapotranspiration. There is no evidence for the presence of an older formation water.

6.2.7 *Minor and trace elements*

Trace elements are generally present at low concentration (Figure 5.5) in the Plylimon groundwaters samples, reflecting the unreactive nature of the bedrock, limited source in the bedrock and short residence times. The highest concentrations measured were for Fe, Mn and Al. Iron and Mn reach concentrations up to 12 and 1.8 mg l⁻¹ respectively, much higher than current drinking water standards. The higher concentrations are mainly present in deeper reducing waters, but high concentrations are also present in shallow acidic groundwaters due to increased solubility of Fe and Mn at low pH and potentially complexation with organic material derived from the soils. Aluminium is highest in the shallow groundwaters, controlled by increased solubility of Al under acidic conditions. The maximum of 394 µg l⁻¹ is much higher than current drinking water standards. The dominant source of Al is probably from the acidic soils of the catchment.

Strontium concentrations are low in comparison to many aquifers (up to 146 µg l⁻¹), reflecting the lack of carbonate minerals and stability of silicate mineral phases. Barium remains low (up to 33 µg l⁻¹) due to low concentrations in the bedrock. Many metal species (Co, Ni, Zn, Pb) are low but do correlate with Fe and/or Mn implying a control by adsorption-desorption, but also reflecting low concentrations in the bedrock. The importance of enhanced concentrations of Ca and metals in stream waters of this area (Shand et al., 2005) has been related to the influence of former mining, but the groundwaters studied are outside this sphere of influence.

The groundwaters from the Wye and the Severn were relatively similar in terms of trace elements concentrations, but with slightly higher median Al and Sr in the forested Severn and higher median Fe and Mn in the Wye where Drift deposits are better preserved.

The halogen elements Br and I reflect atmospheric inputs. Fluoride concentrations are relatively low and probably derived from phosphatic nodules present locally in the sediments.

6.2.8 Temporal variations

There are no long term records of groundwater quality in these catchments. Monthly monitoring of shallow groundwaters over a period of one year (Figure 6.8) showed that there was little variation in most solute concentrations, and those that differed could be due to sampling procedure (Shand et al., 2005).

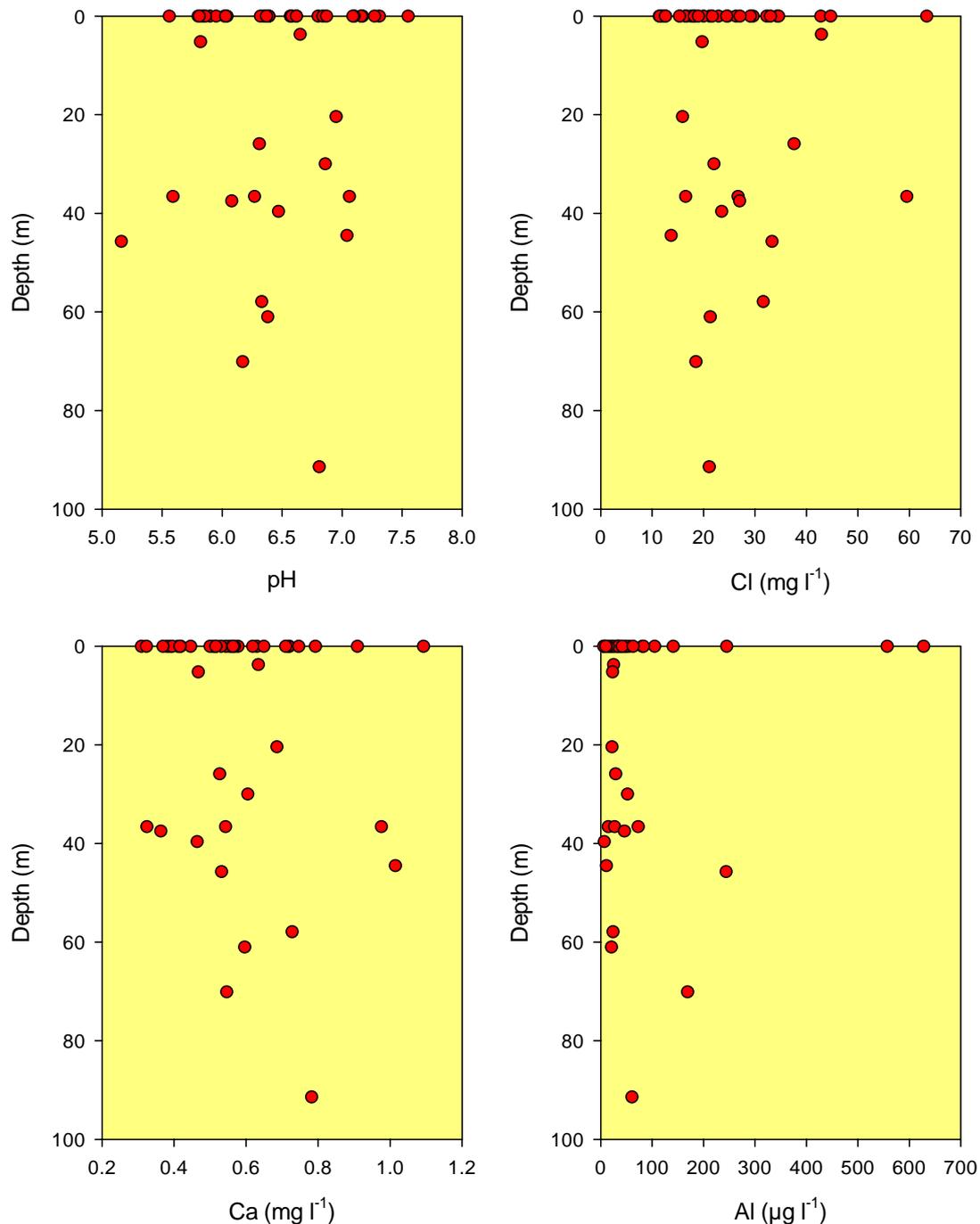


Figure 6.8 pH, Cl, Ca and Al plotted against depth of borehole in the Teifi Valley ground waters. Springs are plotted at zero depth.

6.2.9 Age of the groundwater

Groundwater from both the Severn and Wye catchments were analysed for CFC's and SF₆ (Shand et al., 2004). In the Severn catchment, calculated ages for the shallow boreholes produced ages of ca. 10 years and for the deeper boreholes ca. 45 years. However, the shallow groundwaters showed seasonal variations between summer and winter inconsistent with such data: the shift implied that at least a proportion of the shallow groundwater was, at most, less than 6 months old. The CFC ages for the deeper waters are considered to be real, but the shallow ages are considered to represent mixing of an older and younger groundwater. More recent CFC and SF₆ data for the Wye catchment (BGS, unpublished data) confirm this conclusion. It is likely that the age of groundwater in these catchments varies from hours (Haria & Shand, 2004) to several decades.

6.3 Teifi groundwaters

The Teifi groundwaters cover a much larger area than those presented from Plynlimon (Figure 3.9), but less detail is available on depths and screened intervals. They are used to highlight data in the lower reaches of one of the large rivers draining the Ordovician and Silurian of Wales and the effect of the Drift composition on water chemistry.

6.3.1 Depth variations in hydrochemistry

The depth of most of the boreholes was not known. Solute concentrations and physicochemical parameters show little variation when plotted against depth of borehole (Figure 6.8). However, the screened intervals were not known and it is likely that the sampled water represents a mixture of waters from different depths.

6.3.2 Spatial variations in hydrochemistry

There are relatively large variations in chemistry in the Teifi catchment. Most solute concentrations and SEC are similar in the eastern part of the catchment which is dominated by Welsh Drift. In the west, there are increases in the concentration of a number of solutes (Figure 6.9). The increase in the west includes the major elements Na, Mg, Ca, Cl, HCO₃ and SO₄, and minor and trace elements including Br, I, Li, Sr. The increase in Na, Cl, Br and I, is most likely explained by enhanced sea-salt inputs closer to the sea, a feature also of stream waters close to the western coast of Wales (British Geological Survey, 1999; Shand et al, 1999b). Such elements, when normalised to Cl do not display such trends, consistent with control by such a marine source.

The large increase in Ca (Figure 6.9), Mg and Sr cannot be accounted for by sea-spray inputs. These elements still show a marked increase in many samples in the west of the area when the atmospheric input is deducted. The increase does not relate to changes in bedrock geology, but occurs where the source of Drift changes from Welsh (Ordovician/Silurian dominated) to Irish Sea Drift which contains abundant carbonate shelly material. The increase in these elements is therefore, likely to be controlled by groundwaters dissolving carbonate material during recharge.

Aluminium concentrations tend to be slightly higher in the eastern part of the catchment. It is probable that calcite dissolution (increasing pH) limits the solubility of Al in recharge waters in the west of the area. Nitrate concentrations (Figure 6.9) do not show a simple pattern. The highest concentrations are likely to be due anthropogenic impacts as these are typically enhanced around urban areas or close to farms.

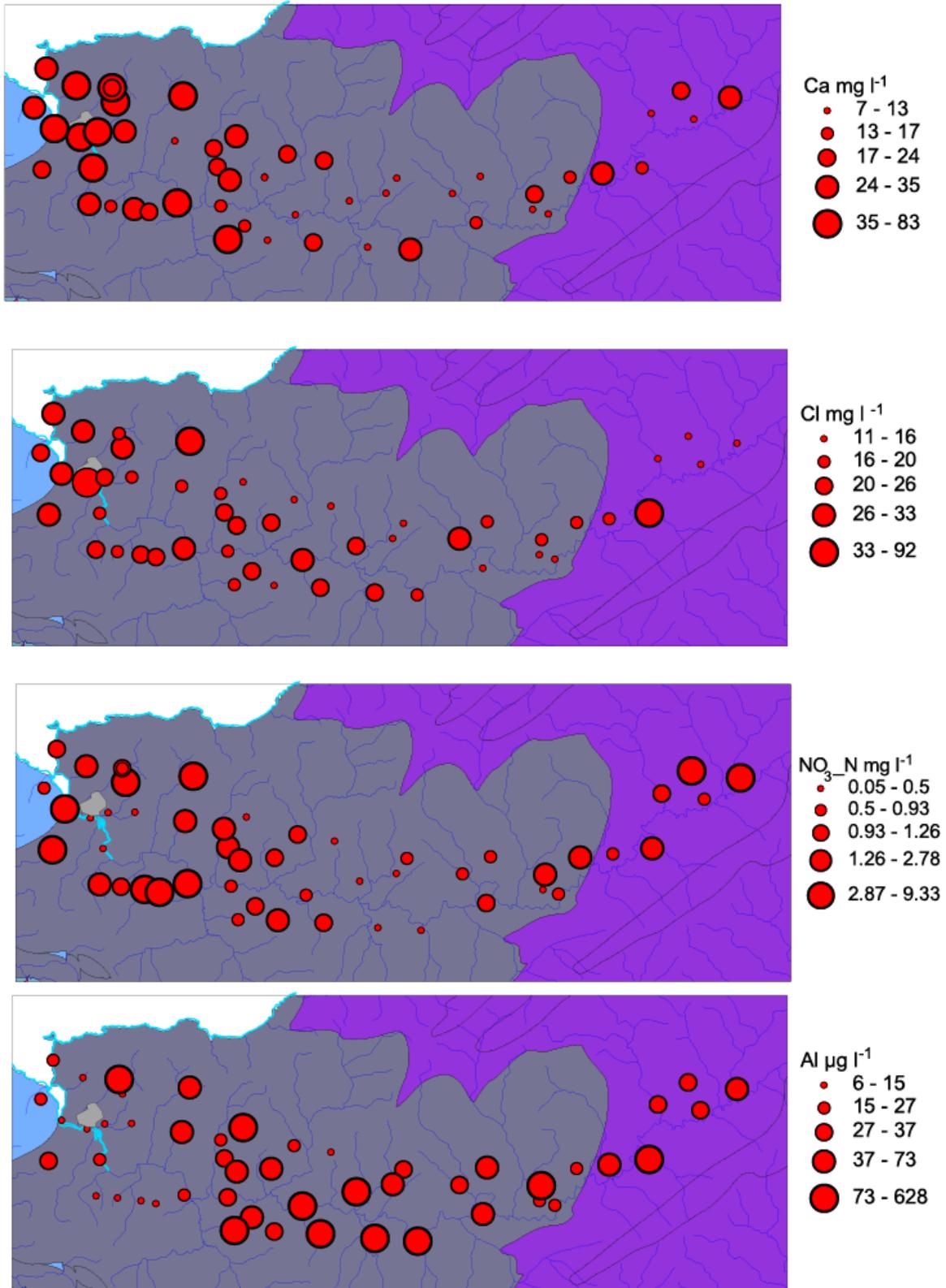


Figure 6.9 Spatial variations in selected elements (Ca, Cl, NO₃ and Al) for the Teifi catchment.

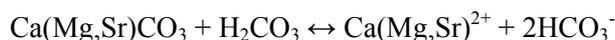
6.3.3 Mineral dissolution reactions

The SEC of the Teifi catchment groundwaters shows as wide a range as those in Plynlimon but with higher values. This is likely to reflect longer residence times in the larger Teifi catchment, as well as the larger number of deeper boreholes. The higher median SEC in the superficial deposit groundwaters, as well as major element concentrations (Table 5.3), shows that weathering rates are higher in these deposits Drift (although there is considerable overlap).

As in the Plynlimon catchments, the dominant minerals in the mudstones and shales are an iron magnesium chlorite, sericite/illite and quartz with lesser amounts of iron oxide, all of which weather slowly. A comparison of major elements with Cl shows that a significant proportion of the Na is derived mainly from rainfall. However, individual groundwaters have Na/Cl ratios slightly greater than 1, indicating a catchment source of Na. The source of the water-rock-derived Mg and Fe is likely to be dominantly from the dissolution of chlorite. A general correlation between Mg and Si also indicates a dominant evolution by silicate dissolution.

The main source of K is likely to be from dissolution of K-feldspar or possibly illite, but the kinetics of dissolution of illite are likely to be slow. The range of K concentrations is typically between 1-5 mg l⁻¹, two groundwaters with much higher K (9 and 17 mg l⁻¹) are considered to be polluted (NO₃-N > 7 mg l⁻¹).

The main source of Ca in drift-free areas is likely to be from dissolution of feldspar, although it is possible that calcite may be present locally in veins. The increase in Ca, Mg and Sr in the west of the catchment is due to carbonate dissolution from the often abundant shelly material in the overlying Irish Sea derived Drift deposits:



This reaction consumes acidity and may, therefore, affect the reaction rates and solubility of a number of other solutes.

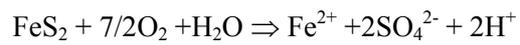
6.3.4 Redox reactions

Many of the groundwaters in this study were sampled via storage tanks or from springs, therefore the redox measurements are not likely to be representative of the groundwaters. In addition, many of the waters sampled may be mixtures of water from different fractures, making interpretation of redox status difficult.

Concentrations of Fe and Mn are typically present at low concentrations (Table 5.4) indicating that the groundwaters are generally oxidising. In the drift groundwaters, Fe was below the limit of detection. Several spring waters did contain moderately high Fe and Mn (Figure 5.10), significantly above European Drinking Water limits (200 and 50 µg l⁻¹ respectively). The spring with the highest Fe (720 µg l⁻¹) was slightly acidic (pH 6.02) and contained high K, P and NH₄-N, and it is possible that pH and organic-complexation play an important role in the transport of Fe. Iron and Mn oxyhydroxides form important controls on many trace elements (e.g. Co, Cr, Cd): in oxidising waters, these mineral phases limit the concentrations due to adsorption (especially at higher pH) or they may release such metals because of reductive dissolution under reducing conditions. There is a tendency for the higher Fe waters to contain higher concentrations of some metals (Figure 6.10) indicating that reductive dissolution may be important, but there is considerable scatter, probably reflecting other processes such as removal of Fe during oxidation or spatial variations in source.

The general oxidising nature of the aquifer is also indicated by the presence of NO₃-N: nitrate is stable only when oxygen is present in the groundwater. Groundwaters with high nitrate typically have low Fe concentrations (Figure 6.10).

The dominant source of geogenic SO_4 is from the oxidation of pyrite (FeS_2):



Pyrite is present in many of the mudstones and shales of the catchment, and in the absence of calcite or other acid neutralising mineral phases, pyrite oxidation will cause acidification of groundwater.

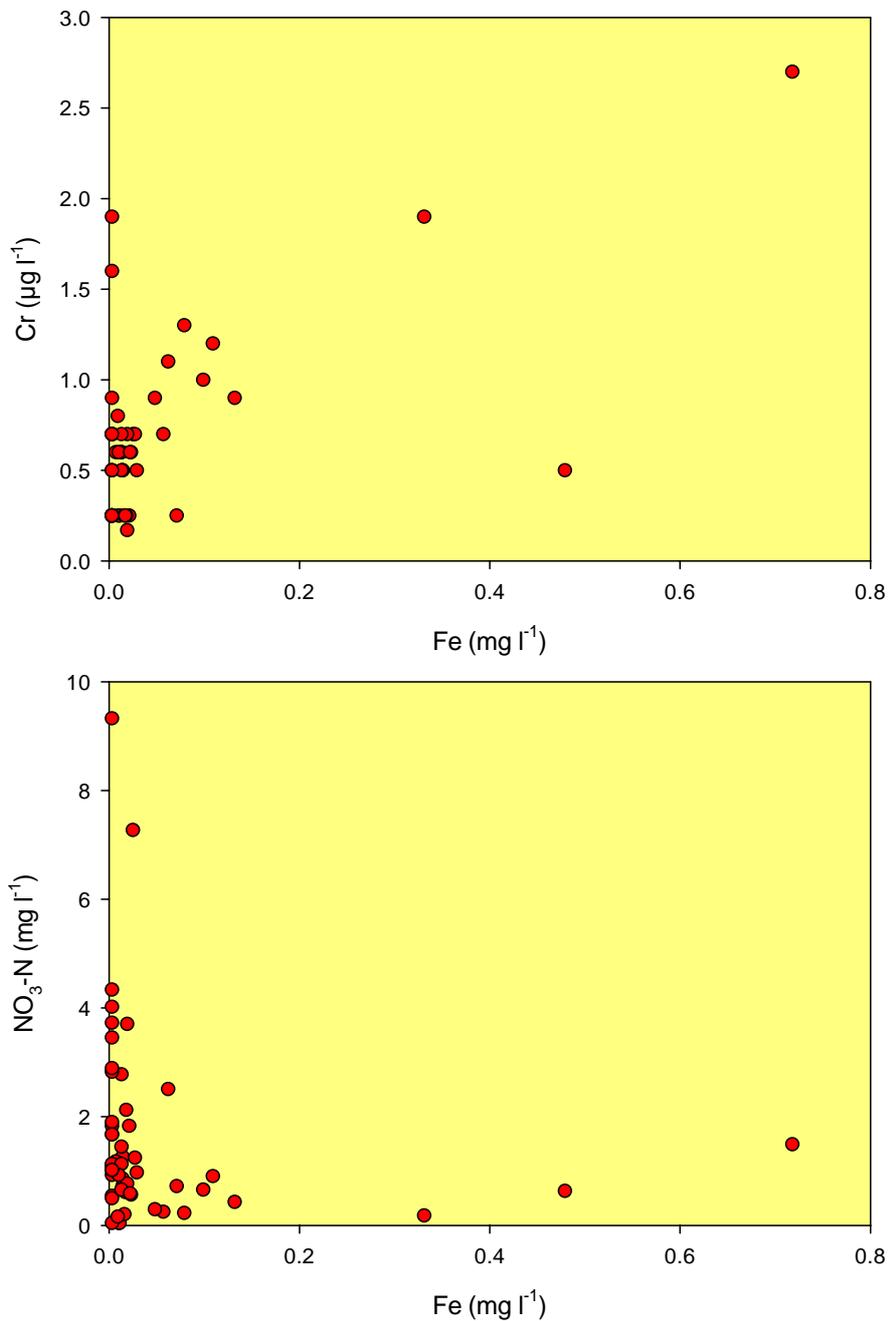


Figure 6.10 Plots of Cr and $\text{NO}_3\text{-N}$ against Fe concentration in the Teifi groundwaters.

6.3.5 *Ion exchange reactions*

There is little evidence for ion-exchange reactions being a significant process in the groundwaters of the Teifi catchment.

6.3.6 *Mixing with older formation water*

Chloride concentrations are higher (median Cl of 22 mg l⁻¹) than those at Plynlimon (median Cl of 5.7 mg l⁻¹). Higher Cl concentrations are to be expected in groundwaters in the west of the Teifi Valley due to the closer proximity to the sea (Shand et al., 1999b; British Geological Survey, 1999). However, it is likely that many groundwater compositions have been modified due to anthropogenic factors such as urbanisation, road salt application, septic tank leakage or agricultural inputs. The sample with highest Cl, for example, was from a borehole abstracting water from beneath made ground in Cardigan. The Br/Cl ratio for this sample is much lower than seawater indicating a component of non-marine origin. The majority of groundwaters are not significantly enhanced above concentrations expected of rainfall-derived Cl modified by evapo-transpiration. The superficial deposit groundwaters have a similar range in Cl to the bedrock samples (Figure 5.7). It is therefore considered that mixing with an older formation water is not important in this area.

6.3.7 *Trace elements*

Trace elements are generally present at low concentration (Figure 5.10) in the Teifi groundwater samples, reflecting the unreactive nature of the bedrock and probable short residence times. The highest median concentrations were for Sr, Al and Fe (Figure 5.10). Dissolved manganese concentrations were up to 2.4 mg l⁻¹, much higher than current drinking water standards. Aluminium, which reached concentrations up to 628 µg l⁻¹, does not correlate with pH, but is highest in some of the spring samples. This lack of correlation may simply be due to mixing close to spring discharges or to borehole construction e.g. large screened sections mixing deep and shallow groundwater in the borehole column. Many metal species (Co, Ni, Zn, Pb) are also low reflecting the generally oxidising nature of the groundwater as well as low concentrations in the bedrock.

Strontium concentrations are higher than in the Plynlimon groundwaters (up to 640 µg l⁻¹, compared with 146 µg l⁻¹ in Plynlimon). The good correlation of Sr with Ca implies that the source is from calcite. Barium remains low (median of 6 and 23 µg l⁻¹ in the bedrock and drift aquifers respectively) due to low concentrations in the bedrock.

6.3.8 *Temporal variations*

There are no long term records of groundwater quality in these catchments.

6.3.9 *Age of the groundwater*

The stable isotope compositions (Table 5.3) of the groundwaters in both bedrock and Drift deposits are consistent with a Holocene to modern age, but there are no direct age determinations of groundwater in the Teifi catchment to constrain the ages further.

6.4 **Rheidol groundwaters**

The Rheidol groundwaters cover a relatively large area from the upper reaches of the catchment down the valley towards Aberystwyth (Figure 3.15 and 3.17). Most groundwaters in bedrock were sampled from springs, with only one borehole available for sampling. The four samples from the superficial gravel deposits will be compared to those from the group of bedrock +/- Drift samples.

6.4.1 Depth variations in hydrochemistry

Depth variations in the bedrock groundwaters could not be assessed due to the lack of boreholes. Two piezometers were sampled from the borehole in gravels at Trering (6 and 23 m depth). The two boreholes were similar in terms of most parameters including SEC, DO Ca, Mg, Na, NO₃-N (7-10 mg l⁻¹) and Cl, but the deeper piezometer had slightly higher HCO₃, Si and Li and slightly lower K, NO₃ and Ba. An adjacent borehole (ca. 20 m distant with a depth of 26 m) was more reducing (DO <0.1 mg l⁻¹ compared to 3 mg l⁻¹ in the piezometers) with much lower NO₃-N (0.6 mg l⁻¹) and high Mn (1110 µg l⁻¹ compared to < 6 µg l⁻¹). This highlights the strong spatial as well as depth variations in the gravel aquifer.

6.4.2 Spatial variations in hydrochemistry

The spatial variations for selected solutes are shown on Figure 6.11. The groundwaters from springs on Ordovician bedrock in the north east of the area tend to have low concentrations of most major elements derived from water-rock interaction. It is possible that the lower concentrations reflect the mineralogy of the Ordovician bedrock, but they could also result from other factors such as shorter residence time or soil type. These groundwaters also show elevated Al concentrations (Figure 3.10).

The groundwaters sampled from the Llandoverly rocks do not show any consistent pattern (Figure 3.10). The groundwaters are likely to be controlled by local flow systems, hence heterogeneity is likely to be the norm for the hydrochemical characteristics in such aquifers. Nitrate concentrations are much higher in some samples than expected, due to localised anthropogenic inputs.

6.4.3 Mineral dissolution reactions

The SEC of the Rheidol catchment groundwaters shows a wide range (Table 5.5), most likely reflecting variable residence times. The moderately high median SEC and major elements in the gravel aquifers (Table 5.5), indicate that the degree of weathering is similar to many of the higher TDS springs from bedrock.

As in the Plynlimon and Teifi catchments, the dominant minerals in the mudstones and shales are iron magnesium chlorite, a sericite/illite and quartz with lesser amounts of iron oxide, all of which weather slowly. The lack of carbonate minerals in the bedrock has given rise to groundwaters with lower maximum SEC and Ca concentrations in comparison with those present in the Teifi Valley (Table 5.3). A non-carbonate source of Ca and HCO₃ is also indicated by the very light ¹³C signatures (δ¹³C ‰ from -17 to -19). A comparison of major elements with Cl shows that most of the Na is derived mainly from rainfall, whereas most of the Ca and Mg are derived from water-rock interactions. The source of the water-rock-derived Mg and Fe is likely to be dominantly from the dissolution of chlorite. There are general correlations between Si and the major cations Ca, Mg and Na (above that derived from rainfall) which indicate that silicate rather than carbonate dissolution is most likely the dominant source of major cations.

The increase in SO₄ along with Si is likely to be due to increased weathering caused by the oxidation of sulphide minerals (section 6.4.4). The main source of K is likely to be from dissolution of K-feldspar or possibly illite, but the dissolution rate of illite is likely to be slow. The range of K is typically less than 2.5 mg l⁻¹, although two groundwaters with much higher K (9 and 10.5 mg l⁻¹) are likely to be polluted.

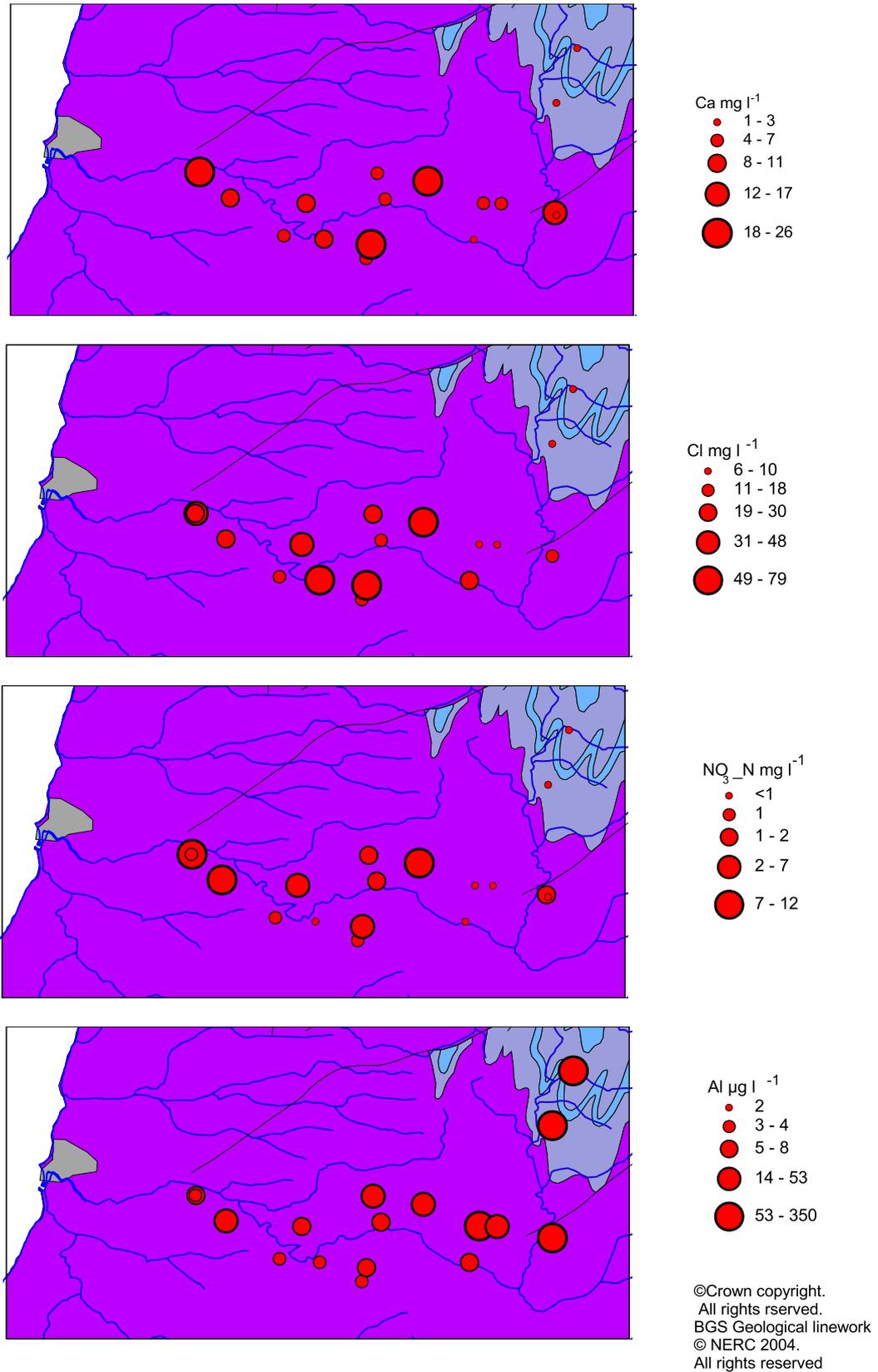
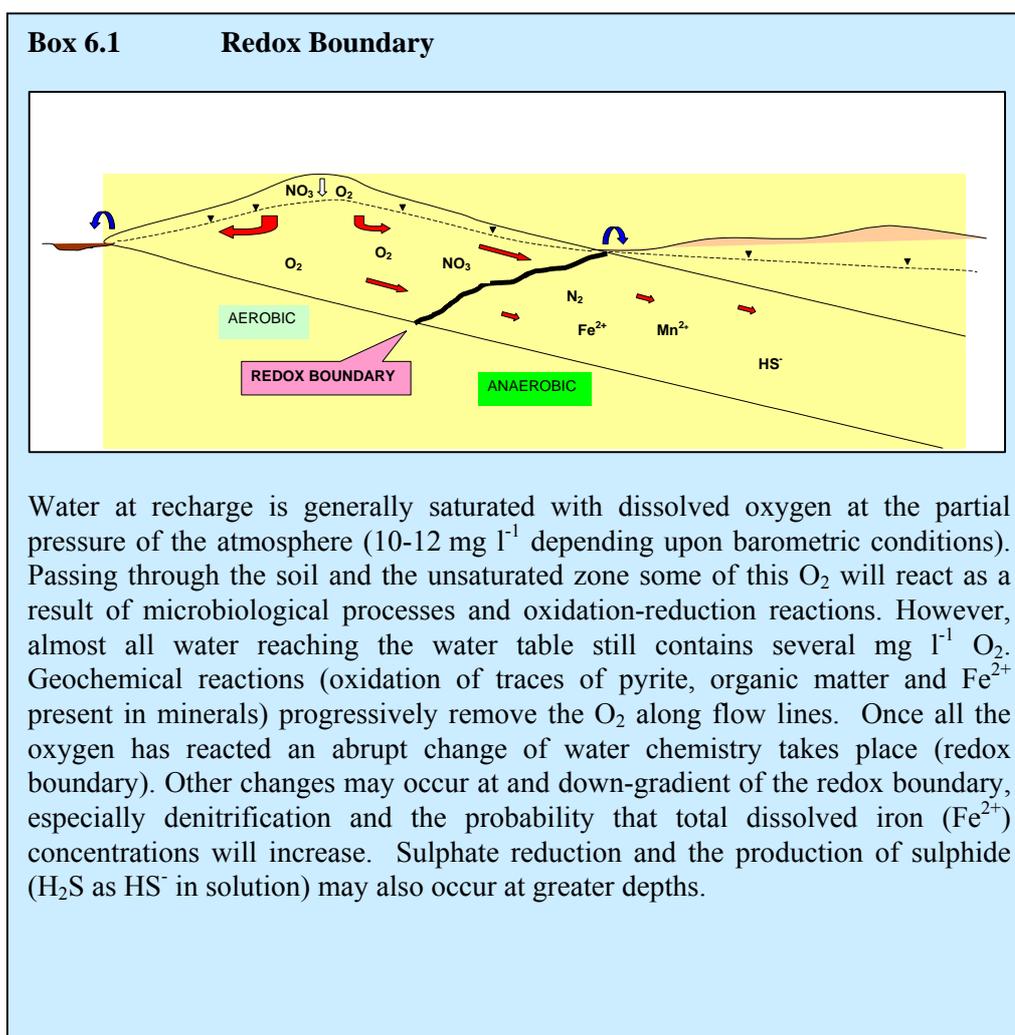


Figure 6.11 Spatial variations in selected elements (Ca, Cl, NO₃ and Al) for the Rheidol catchment.

6.4.4 Redox reactions

Many of the groundwaters in this study were sampled from springs, therefore the redox measurements are likely to have changed rapidly due to contact with the atmosphere. Iron and Mn are typically present at low concentrations (Table 5.6) indicating that the groundwaters are generally oxidising. In the drift groundwaters, Fe was below the limit of detection, but Mn reached very high concentrations, with Ty Llwyd groundwater having more than 6 mg l^{-1} Mn. Several spring waters contain moderately high Fe and Mn (Figure 5.10), significantly above the value recommended by the EC Drinking Water Directive (200 and $50 \text{ } \mu\text{g l}^{-1}$ respectively). Iron and Mn oxy-hydroxides form important controls on many trace elements (e.g. Co, Cr, Cd): in oxidising waters: they may limit concentrations due to adsorption (especially at higher pH) or they may release such metals because of reductive dissolution under reducing conditions. The concentrations of redox sensitive trace metals are generally low reflecting the generally oxidising conditions in much of the aquifer, but tend to be higher where Fe is present.



The general oxidising nature of the aquifer is also indicated by the presence of $\text{NO}_3\text{-N}$: nitrate is stable only when oxygen is present in the groundwater. Groundwaters with high nitrate typically have low Fe concentrations.

The dominant source of geogenic SO_4 is from the oxidation of pyrite (FeS_2) (see section 6.3.4). Pyrite is present in many of the mudstones and shales of the catchment, which in the absence of calcite or other acid neutralising mineral phases will cause acidification of groundwater.

6.4.5 Ion exchange reactions

There is no evidence for ion-exchange reactions being a significant process in the groundwaters of the Rheidol catchment.

6.4.6 Mixing with older formation water

Chloride concentrations are higher (median Cl of 14 mg l^{-1} in the bedrock and 20 mg l^{-1} in the gravels) than those at Plynlimon (median Cl of 5.7 mg l^{-1}). It is likely that many groundwater compositions have been modified due to anthropogenic factors such as urbanisation, road salt application, septic tank leakage or agricultural inputs. The slightly higher Cl in the drift groundwaters may reflect slightly greater contamination. The majority of groundwaters, are not significantly enhanced above concentrations expected of rainfall-derived Cl, modified by evapo-transpiration, and mixing is not considered important. It is therefore considered that mixing with older formation water is not important in this area.

6.4.7 Trace elements

Trace elements are generally present at low concentration (Figure 5.16) in the Rheidol groundwater samples, reflecting the unreactive nature of the bedrock and probable residence times. The highest median concentrations were for Fe, Al and Zn (Figure 5.16). The sample with highest Zn ($210 \text{ } \mu\text{g l}^{-1}$) also had the highest SEC, Ni, Cu and SO_4 , and these enrichments may be due to sulphide oxidation. Aluminium reached concentrations of $350 \text{ } \mu\text{g l}^{-1}$ in some of the more acidic groundwaters, but is low above pH ca. 6.2.

Median Sr concentrations were lower ($74 \text{ } \mu\text{g l}^{-1}$) than in the Plynlimon ($146 \text{ } \mu\text{g l}^{-1}$) and Teifi ($640 \text{ } \mu\text{g l}^{-1}$) areas. This may reflect a different mineral assemblage (e.g. lesser calcite or plagioclase) or reflect the lack of samples from groundwaters which may have had a longer residence time. Barium remains low (median of 3.1 and $2.8 \text{ } \mu\text{g l}^{-1}$ in the bedrock and drift aquifers respectively) due to low concentrations in the bedrock.

6.4.8 Temporal variations

There were no long-term records of groundwater quality in the Rheidol catchments available.

6.4.9 Age of the groundwater

The stable isotope compositions (Table 5.5) of the groundwaters in both bedrock and Drift deposits are consistent with a Holocene to modern age. The three samples from the gravel aquifers at Ttering (NGR 263142 280544) were sampled for CFC's and SF_6 in order to estimate residence times better.

The sulphur hexafluoride data has been adjusted for the incorporation of 9% 'excess air', for which this determination is particularly sensitive to. The results are shown in Table 6.1.

The CFC-12 and SF_6 data from two piezometers in borehole B (B1 at 6 m depth and B2 at 26 m depth) did not provide a consistent age suggesting that mixing has occurred. The data fit approximately to a two component groundwater mixing model with the shallower sample (BH B1) containing approximately 50% modern water, and the deeper sample 20-40% modern water. Sample

BH A was consistent with a piston flow model of groundwater movement and has an approximate groundwater age of 26– 31 years, equivalent to a recharge year between 1973 and 1978.

Table 6.1 CFC and SF₆ data for groundwaters in glaciofluvial gravels at Trering.

Site	CFC-12	CFC-11	SF ₆	CFC-12	CFC-11	SF ₆	CFC-12	CFC-11	SF ₆
	pmol/l		fmol/l	Modern Fraction			Recharge Year		
Trering BH B2	0.63	1.97	0.90	0.21	0.35	0.39	1969	1973	1989
Trering BH B1	1.58	4.87	1.14	0.53	0.86	0.49	1979	1987	1992
Trering BH A	0.95	1.37	0.26	0.32	0.24	0.11	1973	1971	1978

The age/mixing data implied by the CFC/SF₆ analyses are therefore consistent with hydrochemical data in implying both vertical and lateral heterogeneity in gravel aquifers over short distances.

7. BASELINE CHEMISTRY OF THE AQUIFERS

The baseline chemistry of groundwater in an aquifer is determined by a range of physical as well as chemical processes. The primary input to most major aquifers is rainfall, although connate or formation water may be present in parts of the aquifer where flushing has not been complete. In addition, leakage from underlying or overlying aquifers may modify the groundwater chemistry either locally or regionally. A series of chemical reactions takes place during recharge and groundwater flow, the most important being mineral dissolution and precipitation, mixing, redox reactions, ion exchange and sorption/desorption reactions. Water-rock interaction is complicated because most aquifers are heterogeneous in terms of mineralogy and geochemical environment (e.g. redox status). Many chemical reactions are also time-dependent and this gives rise to a range in baseline chemistry as the groundwaters move from areas of recharge to discharge.

Superimposed on this “natural” baseline are anthropogenic influences. These include point-source and diffuse pollution which directly modify the baseline chemistry. However, the baseline can also be modified indirectly, for example, by abstraction: this can induce leakage from overlying units or upconing of deeper water of a different chemical composition. Although such changes can occur where the introduced solutes are derived “naturally”, and therefore represent baseline, the aquifer or unit being characterised has been modified, hence the need to define the baseline of a specified system.

In the present study, boreholes which were known to be affected by point-source pollution have not been sampled. However, many groundwaters especially where the aquifer is unconfined, show signs of diffuse pollution, dominantly from agricultural activities and these have been included. The determination of baseline in such cases can be determined from historical records, (in this study, only available for the Plynlimon catchments), by comparing with pristine areas, applying statistical techniques or modelling. Most of these techniques have limitations and should be used together to provide a reasonable estimate of the baseline composition (Shand & Frengstad, 2001).

The three areas selected for this study are different in terms of anthropogenic impacts. The headwaters of the Severn and Wye are remote and not impacted by urbanisation or intensive farming. In the Teifi Valley, urbanisation may have impacted on the groundwater locally and many groundwaters were sampled from farms where agricultural impacts may be present. The Rheidol is similar in many ways to the Teifi Valley, with additional impacts from previous Pb-Zn mining.

In the Plynlimon catchments, land use in the Hafren catchment is largely dominated by managed forest. In contrast, the Wye catchment is managed grassland dominated by sheep farming. The groundwaters in both catchments, however, do not appear to have been largely impacted by direct anthropogenic inputs. However, the impact around old Pb-Zn mines is likely to be large. The lower reaches of the headwaters of the Wye underwent improvement in the early part of the century by liming, but this area is downstream of the groundwaters sampled. The Wye, therefore, represents the most pristine of the areas discussed. However, the area cannot strictly be described as totally pristine due to sheep farming and inputs of modern atmospheric pollution. Nevertheless, concentrations of N-species are low (Table 5.1), limited by uptake of atmospheric-N by vegetation and denitrification within the soils and groundwater. Nitrate concentrations in many of the Wye groundwaters are much lower than found in many UK aquifers, and for practical purposes can be classed as baseline (the upper baseline, assessed as the 97.7 percentile, is $0.64 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$). Maximum nitrate concentrations are slightly higher in the Hafren catchment (Table 5.1). However, NO_3 increased in groundwater after felling (Neal et al., 2003). The shallower groundwaters have, therefore, been impacted to a small degree by land management practices. The slightly higher median concentration for P and K in the Severn catchments may be due to previous application of fertiliser, but the highest concentrations of P were found in the Wye groundwaters (reflected in a higher upper baseline), most likely derived from phosphate concretions in the bedrock. The slightly higher median Cl and Al may

also be due to forestation, caused by scavenging of atmospheric salts and acidification of soils respectively. Although the groundwater chemistry in many of these young (up to several decades old), shallow groundwaters does not strictly represent baseline, it could be argued that for practical purposes they are sufficiently close to be classed as such. The baseline is largely determined by silicate dissolution reactions and varies both with depth and spatially over the catchments. This is likely to be typical of all the areas studied due to the dominance of fracture flow in the bedrock.

The median and maximum concentrations of NO_3 in the Teifi groundwaters (both bedrock and drift) are significantly greater than in the Plynlimon catchments. This is mainly a reflection of differences in land-use, agriculture and the greater degree of more urban populations. The Teifi Valley is larger than the headwater areas studied at Plynlimon and contains a greater abundance of superficial deposits. The lack of good historical data, however, makes it difficult to assess the baseline of the region. The highest NO_3 concentrations are likely to be anthropogenic in origin. Inspection of elements typically associated with pollution (NO_3 , NH_4 , P, K) shows that these elements are often closely correlated e.g. the sample with the highest P ($1670 \mu\text{g l}^{-1}$) also contained high $\text{NH}_4\text{-N}$ (1.7 mg l^{-1}) and K (34 mg l^{-1}). It is concluded that the groundwaters of the Teifi have been locally impacted by N-species, K, Na, Cl, P and organic carbon. There is a change in the populations of NO_3 on probability plots (Figure 5.8) at 0.6 mg l^{-1} (similar to the upper baseline for the Wye catchment (Table 5.1) and 4 mg l^{-1} which may discriminate baseline from diffuse and point source contamination. However, the non-conservative behaviour of N-species makes the use of such plots difficult to interpret. For most other elements in the groundwaters studied, it is likely that concentrations are close to baseline. In the east the baseline is largely determined by silicate dissolution reactions. This baseline changes towards the western parts of the aquifer due to the presence of carbonate-bearing Irish Sea Drift in the west. This has given rise to higher baseline concentrations for Ca, Mg, HCO_3 and Sr, explaining the two populations of data, especially for HCO_3 and Sr on cumulative probability plots (Figures 5.8 and 5.10). As for the Plynlimon catchments, the baseline is also likely to vary spatially and with depth within these regions due to the fractured nature of the aquifer.

The baseline chemistry of the Rheidol groundwaters, with generally lower TDS, reflects the dominance of spring sources with lower solute concentrations. Residence times are thus likely to be short. Most of the springs sampled were located upslope of dwellings and farms, hence point source pollution is less of a problem. Only two springs had nitrate greater than $4 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$. The higher nitrate groundwaters also tend to have higher K, but P shows little variation. Two of the four groundwater samples from the gravel aquifer had high nitrate (7.4 and $10.5 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$), the other two were reducing with $\text{NO}_3\text{-N} < 0.1 \text{ mg l}^{-1}$. There were no long-term records for groundwaters in the catchment to assess baseline concentrations of nitrate. There is possibly a shift in population on the cumulative probability plot (Figure 5.14) at ca. 2 mg l^{-1} which could be interpreted as related to pollution, but the number of samples is small. The gravel aquifers are within the range of the bedrock +/- superficial deposits and it appears that the dominant baseline chemistry is controlled by silicate dissolution reactions.

Taken as a whole, the hydrochemical data show that, even in relatively pristine areas such as upland Wales, it is difficult to find true baseline conditions. Due to the inert behaviour of the rocks' constituent minerals, acidification caused by atmospheric pollution has had a significant impact. The fractured nature of the bedrock and high transmissivity of the superficial gravels means that these aquifers are at high risk from surface-derived pollution.

8. SUMMARY AND CONCLUSIONS

The chemical compositions of groundwaters present in the Ordovician and Silurian meta-sedimentary rocks of Wales are very variable. This largely reflects the range in residence times and geochemical environment (pH and redox status) within the bedrock. The rocks are dominated by unreactive minerals such as illite, chlorite and quartz, hence many of the groundwaters are only weakly mineralised. The presence, locally, of sulphide and carbonate minerals form an important control on the evolution of the water chemistry. However, the largest variations are likely to occur with depth as highlighted in the Severn and Wye catchment groundwaters. Many private boreholes are thought to abstract waters from a variety of fractures at different depths, hence the samples collected will be mixtures of waters of contrasting chemistry. The groundwaters are likely to be relatively young varying in age from weeks/months to a few decades, as indicated by the few ages available.

The chemistry of the groundwater varies from very dilute waters dominated by Na, Cl and SO₄ (reflecting an important atmospheric input) to Ca-HCO₃ and mixed types. They vary from acidic to alkaline (pH 4.9 to 8.8) and from oxidising to reducing (Eh -79 to 514 mV). The pH is largely controlled by the degree of water-rock interaction, sulphide oxidation (producing acidity) and carbonate dissolution (producing alkalinity). The dominant process in most groundwaters is silicate dissolution, due to the lack of carbonate minerals present in the bedrock. In the western part of the Teifi Valley, the occurrence of carbonate shelly debris and calcite in the Irish Sea-derived drift has had a marked influence on the concentrations of Ca, Mg, HCO₃ and Sr. Small differences between the chemistry of groundwaters in forested and moorland areas can be attributed to the effect of vegetation in scavenging atmospheric inputs or land management practices.

Groundwater samples collected from superficial deposits are similar to and contain solutes that are generally within the range of the bedrock samples. The relationship between groundwaters in the bedrock and those in the superficial deposits and rivers is poorly understood in the study areas. Although the storage and yields are likely to be small in the bedrock, they have an important role in providing water and solutes to the rivers of these hard rock catchments. The rivers in many parts of Wales have been impacted by former mining activity, and the buffering role of groundwater is likely to be important to the health of ecosystems in the rivers. The aquifers themselves are susceptible to pollution due to the fractured nature of the bedrock and the high transmissivity in the sands and gravels of the superficial deposits.

In general, most of the solutes present in the groundwaters can be interpreted as representing baseline, although small modifications are likely to have occurred due to land management compared with a truly pristine environment. However, several samples showed the effects of anthropogenic inputs in the form of enhanced levels of NO₃, NH₄, P and K, significantly above the baseline.

9. REFERENCES

- Bassett, D.A. 1969 The study of ground water, with particular reference to Wales and the Welsh Border. *Transactions of the Cardiff Naturalists' Society*, **94**, 62-87.
- Brandt, C., Robinson, M. and Finch, J., 2004. Anatomy of a catchment: the relation of physical attributes of the Plynlimon catchments to variations in hydrology and water status. *Hydrology and Earth System Sciences*, **8**(3): 345-354.
- British Geological Survey 1999 *Regional geochemistry of Wales and part of west-central England: stream water*. Keyworth, Nottingham: British Geological Survey.
- Breward, N. 1988 Effect of mineralized faults on stream-sediment geochemistry of an upland catchment at Plynlimon, mid-Wales. *Transactions of the Institution of Mining and Metallurgy* (Section B: Applied Earth Science), **97**, B181-B192.
- Cave, R. & Haines, B. A. 1986 Geology of the country between Aberystwyth and Machynlleth. *Memoir of the British Geological Survey*, Sheet 163 (England & Wales).
- Denaeyer, M.E. 1948 Les gisements de cone-in-cone de France et de Grande-Bretagne (deuxieme partie). *Bull. Belg. Geol. Palaeontol. Hydrol.*, **56**, 382-412.
- Edmunds, W.M., Shand, P., Hart, P. & Ward, R. 2003 The natural (baseline) quality of groundwater in England and Wales: UK pilot studies. *Science of the Total Environment*, **310**, 25-35.
- Fuge, R., Laidlaw, I.M.S., Perkins, W.T., Rogers, K.P., 1991 The influence of acidic and spoil drainage on water-quality in the mid-Wales area. *Environmental Geochemistry and Health*, **13**(2), 70-75.
- Haria, A. & Shand, P. 2004 In press. Evidence for deep sub-surface flow routing in forested upland Wales: Implications for contaminant transport and stream flow generation. *Hydrology and Earth System Sciences*, **8**(3), 334-344.
- Hiscock, K. & Paci, A. 2000 Groundwater resources in the Quaternary deposits and Lower Palaeozoic bedrock of the Rheidol catchment, west Wales. In, N.S. Robins & B.D.R. Mistear (eds.), *Groundwater in the Celtic Regions: Studies in Hard Rock and Quaternary Hydrogeology*. Geological Society, London, Special Publications, **182**, 141-155.
- Hyder Consulting Ltd. 1998 *Lovesgrove Borehole no.2 Rheidol Valley, Ceridigion*. Final Report and Recommendations to Dwr Cymru Welsh Water.
- Kirby, C., Newson, M. and Gilman, K., 1991. Plynlimon research: the first two decades. IH Report No109, Institute of Hydrology, Wallingford.
- National Rivers Authority 1996 *Rheidol, Ystwyth and Clarach Catchment Plan*. National Rivers Authority, Welsh Region.
- Neal, C., Reynolds, B., Neal, M., Hill, L., Wickham, H. & Pugh, B. 2003 Nitrogen in rainfall, cloud water, throughfall, stemflow, stream water and groundwater for the Plynlimon catchments of mid-Wales. *Science of the Total Environment*, **314-316**, 121-151.
- Neal, C., Robson, A.J., Shand, P., Edmunds, W.M., Dixon, A.J., Buckley, D.K., Hill, S., Harrow, M., Neal, M. & Reynolds, B. 1997a The occurrence of groundwater in the Lower Palaeozoic rocks of upland Central Wales. *Hydrology and Earth System Sciences*, **1**, 3-18.

- Neal, C., Wilkinson, J., Neal, M., Harrow, M., Wickham, L. & Morfitt, C. 1997b The hydrochemistry of the headwaters of the River Severn, Plynlimon. *Hydrology and Earth System Sciences*, **1**(3), 583-617.
- Robins, N.S., Shand, P. & Merrin, P.D. 2000 Shallow groundwater in drift and Lower Palaeozoic bedrock: the Afon Teifi valley in west Wales. In, N.S. Robins & B.D.R. Mistear (eds.), *Groundwater in the Celtic Regions: Studies in Hard Rock and Quaternary Hydrogeology*. Geological Society, London, Special Publications, **182**, 141-155.
- Shand, P. & Frengstad, B. 2001 Baseline groundwater quality: A comparison of selected British and Norwegian aquifers. British Geological Survey Internal Report, IR/01/177.
- Shand, P., Darbyshire, D.P.F., Goody, D.C., Edmunds, W.M. & Neal, C. 1997. $^{87}\text{Sr}/^{86}\text{Sr}$ as an indicator of flowpaths and weathering rates in the Plynlimon experimental catchment of Central Wales. *Journal of Conference Abstracts*, **2**(2), 296.
- Shand, P., Darbyshire, D.P.F. & Goody, D.C. 1999a The application of strontium isotopes to catchment studies: The Plynlimon upland catchment of Central Wales. British Geological Survey, *Technical Report* **WD/99/56**.
- Shand, P., Darbyshire, D.P.F., Goody, D.C., Darling, W.G., Neal, C., Haria, A.H. & Dixon, A.J. 2001 The application of Sr isotopes to catchment studies: The Plynlimon upland catchment Central Wales. In, R. Cidu (ed.) *Water-Rock Interaction*, Balkema, 1577-1580.
- Shand, P., Edmunds, W.M., Wagstaff, S., Flavin, R. & Jones, H.K. 1999b Hydrogeochemical processes determining water quality in upland Britain. *Hydrogeology Report Series of the British Geological Survey*.
- Shand, P., Griffiths, K., Darbyshire, D.P.F., Haria, A.H. & Davies, J. 2004 Streamflow generation in upland impermeable catchments – is there a need to think deeper ? In, R.B. Wanty & R.R. Seal (eds.), *Water-Rock Interaction*, Balkema, 1391-1395.
- Shand, P., Haria, A. H., Neal, C., Griffiths, K. J., Goody, D.C., Dixon, A. J., Hill, T., Buckley, D.K. & Cunningham, J. E. In press. Hydrochemical heterogeneity in an upland catchment: further characterisation of the spatial, temporal and depth variations in soils, streams and groundwaters of the Plynlimon forested catchment, Wales. Submitted to *Hydrology and Earth System Sciences*.
- Waters, R.A., Davies, J.R., Wilson, D. & Prigmore, J.K. 1997 A geological background for planning and development in the Afon Teifi catchment. *British Geological Survey Technical Report*, WA/97/36. 102pp.

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