Karst hydrogeology, hydrogeochemistry and processes of tufa deposition in Carboniferous Limestone springs of the Mells Valley, Somerset

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A thesis submitted in partial fulfilment of the requirements of the University of the West of England, Bristol for the degree of Doctor of Philosophy at Bath Spa University

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June 2007

ABSTRACT

A number of karst springs rise in the Carboniferous strata of the Mells Valley, Somerset which is an area surrounded by many active and disused quarries. Some of these karst springs actively deposit tufa, a secondary precipitate of calcium carbonate, and they have been identified by the Environment Agency as potentially vulnerable to the effects of local sub-water table quarrying. A comparative study of a tufa-depositing spring, Whitehole Farm Spring, and a non tufa-depositing spring, St. Dunstan's Well, was carried out in order to determine the influence of hydrogeology, hydrogeochemistry and environmental biology on the processes of tufa deposition. The two springs are approximately 2 km apart and located within the same outcrop of Carboniferous Limestone strata.

A series of qualitative dye-tracing tests established a positive hydraulic connection between a feeder stream which rose in the Old Red Sandstone of the upper hydrological catchment, a sinkhole at the junction with the Lower Limestone Shales and Whitehole Farm Spring resurgence in the Carboniferous Limestone. The sinkhole was shown to have two separate channels to the water table. The tests demonstrated that structural geology and the water table had definable effects on the subterranean route and travel time of the allogenic recharge water. The recharge water to Whitehole Farm Spring was guided by the SE – NW Downhead Fault and did not follow the SW – NE course of the natural dry valley. The water velocity was dependent on the height of the local water table at the time of the tests. Hydrograph analysis of flow data combined with the dye-tracing tests illustrated the rapid response of the springs to storm events (< 24 hrs). The results gave an indication of the shallow nature of the Carboniferous Limestone aquifer and the different stages of development of fissures and conduits in the two spring systems, St. Dunstan's Well being a more mature karst system than Whitehole Farm Spring.

Analysis of 18 monthly water samples from both springs at their resurgences and 100 metres downstream revealed temporal and spatial differences in the hydrogeochemistry of the springs and their streams. Ca^{2+} and HCO_3^- were the dominant ions in both spring waters, however, neither of the spring resurgences were supersaturated with respect to calcite (Whitehole Farm Spring, mean -0.17 ± 0.08 SIc ; St. Dunstan's Well, mean -0.33 ± 0.08 SIc). The resurgence water at Whitehole Farm Spring was higher in Ca^{2+} (mean 112 ± 3.35 mg l^{-1}) than at St. Dunstan's Well and became supersaturated as it flowed downstream (mean 0.43 ± 0.10 SIc). Lower Ca^{2+} levels at St. Dunstan's Well (80 ± 2.7 mg l^{-1}) were influenced by the degassing of recharge water and the deposition of calcite as speleothem within the open system of caves behind the resurgence. Downstream supersaturation was also lower (-0.011 ± 0.079 SIc). There was a highly significant difference ($p < 0.001$) between mean daily flow at Whitehole Farm Spring (0.95 ± 0.19 ML d^{-1}) and St. Dunstan's Well (11. 58 ± 1.93 ML d^{-1}). Electrical conductivity, total dissolved solids, alkalinity, Na, K, and NO_3 were also higher at Whitehole Farm Spring, the differences being significant ($p < 0.01$).

There were major differences in the biodiversity and environment of the two sites. Petrographic examination of field-collected tufa samples from Whitehole Farm Spring demonstrated that the stream flora, in particular lower plants, and the surrounding riparian vegetation were a major influence on the formation and morphology of the tufa deposits. Newly accreted tufa which had formed on artificial substrates placed in the stream, revealed calcite crystals surrounding the empty moulds of filamentous cyanobacteria. Hydrological conditions within the stream also influenced the micromorphology of calcite crystals forming on two filamentous algal species, *Vaucheria longata* and *Zygnema stellinum*.

Whitehole Farm Spring was also found to be the more stable environment where biodiversity was higher. The shaded conditions created by Whitehole Farm Spring's woodland environment were beneficial to the growth of filamentous algae, cyanobacteria and bryophytes. The dominant species upstream was a crustose epilithic red alga *Hildenbrandia rivularis*. Downstream, in and on the tufa deposits the dominant aquatic flora were a number of species of the filamentous yellow-green alga *Vaucheria* and the cyanobacterium *Lyngbya* and the moss species *Palustriella* (*Cratoneuron*) *commutatum*. These species were either absent or growing under different ecological conditions at St. Dunstan's Well where there was sparse woodland. The dominant species at St. Dunstan's Well was the filamentous green alga *Cladophora glomerata* which was not present at Whitehole Farm Spring. Debris from the surrounding riparian vegetation at Whitehole Farm Spring acted as substrates for colonisation by microorganisms which enhanced the nucleation and growth of tufa in the stream. Hydrological and environmental conditions at St. Dunstan's Well prevented the accumulation of organic debris within the stream flow. The study highlighted the need for conservation of the natural environment and biota in order to maintain actively-depositing tufa springs.

ACKNOWLEDGEMENTS

The funding for this project was provided by Hanson Quarry Products, Europe and the Environment Agency and I would like to express my gratitude to Malcolm Keeble (Hanson), Martin Crow (Hanson), Pauline Johnstone (EA) and Paul Whittaker (EA). In particular, I would like to thank Roger Griffiths (Hanson) a valued friend and colleague, for his support and patient understanding throughout the period of this study.

I am also grateful to Prof. Alan House and Dr. Nick Rukin (Entec) for taking part in the Steering Group meetings.

I would like to thank my supervisors Dr. Juliet Brodie (Natural History Museum) and Dr. Nigel Chaffey (Bath Spa University) for their help and advice on all sections of the text. I would also like to thank Dr. Anil de Sequira (Bath Spa University), Mr. Allan Dyson (Bath Spa University), Dr. Gill Odolphie (Hanson) and Dr. Mary Holmes for their helpful advice and literary contributions.

Many thanks to Mr. Hugh Prudden, Dr. Willie Stanton and Prof. Eric Robinson (Somerset Geology Group) for their encouragement and enthusiasm for the project (and inside information on the Mendip Hills!).

I am grateful to Prof. Brian Whitton and Dr. David John for their assistance with species identification at the Freshwater Algal Identification workshop, University of Durham.

A special mention must go to my brother Nick, for retrieving hundreds of lost files when my ancient computer suddenly and unexpectedly expired. How did he do it?

I am indebted to Dr. Clem Maidment, also a valued friend and colleague, for all his help as my voluntary external supervisor, German translator and general sounding board.

Finally, and most of all, I want to thank my partner and uncomplaining field assistant, Alan, who has supported me in every way during my academic and scientific career.

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INTRODUCTION

1.1 BACKGROUND TO THE STUDY

Dewatering is a common practice carried out by the mineral extraction industry to ensure the dry working of a quarry, but the practice also has the effect of lowering the local water table. The possible disturbance, or derogation, of flow in springs and surface watercourses caused by quarrying operations, and the impact on dependent flora and fauna is controlled by conditions included in planning consents and abstraction licences issued by the local authority and the Environment Agency (EA). Therefore, as a consequence of environmental regulations and concerns regarding the effects of sub-water table limestone quarrying, the international aggregates company, Hanson plc. (formerly ARC), entered into a S106 Agreement in 1995 with Somerset County Council and the EA as part of the conditional planning permission for an extension to Whatley Quarry, Somerset (NGR ST725 480). S106 refers to Section 106 of the Town and Country Planning Act 1990; River and Spring Augmentation Measures. Under the terms of the S106 agreement, Hanson plc. guaranteed to ensure adequate quality and quantity of water in a number of springs in the vicinity of Whatley Quarry. Some of the springs in the Mells Valley near Whatley Quarry actively deposit tufa and the EA was concerned that any augmentation water would have to be of suitable quality to ensure that tufa deposition was maintained.

Freshwater tufa is a secondary calcium carbonate ($CaCO_3$) deposit which is precipitated from calcium bicarbonate-rich water and is valued globally not only for its unique geomorphological and sedimentological features but also for its specialised active and fossil biota (Viles & Goudie, 1990). Actively-depositing tufa springs have great conservation value as they often contain unique floral and faunal communities dependent on the flowing, carbonate-depositing environment (Pentecost *et al.* 2000). The conservation of tufa-depositing springs is of particular concern and the EC Directive 92/43/EEC Annex 1 (Conservation of Natural Habitats) specifies "petrifying springs with tufa formation" as a priority habitat. Tufa-depositing springs are also included in both the South-West Regional Biodiversity Habitat Action Plan (Cordrey, 1997) and the Mendip Biodiversity Habitat Action Plan (SERC, 1995). Increasing pressure from, for example, industry, agriculture and urbanisation has resulted in the pollution and even cessation of many natural springs (Goudie *et al.*, 1993; Biron, 1999). Climate change has also been implicated in a future decline in tufa deposition as a result of decreased precipitation and reduced rates of limestone dissolution (Viles, 2003). Several authors have suggested that tufa deposition has been in decline in the UK and Europe since the late-Holocene (Goudie *et al.* 1993; Griffiths & Pedley 1995) although this view is challenged by Baker and Simms (1998) who suggested that there had been significant under-reporting of contemporary, active tufa deposition. Actively-depositing tufa springs are vulnerable to environmental changes (Pentecost *et al.,* 2000) which can be climatically and/or anthropogenically induced.

Part II of the Section 106 Agreement (Water Quality Criteria) required a baseline chemical survey of the springs. Detailed hydrochemical surveys were subsequently carried out on behalf of Hanson plc. by Entec UK Ltd from March 1995 to June 1996 and from April 1997 to April 1998. The hydrochemical analyses suggested that water from Whatley Quarry sump could be suitable for augmentation of the non tufa-depositing springs but not suitable for directly augmenting the tufa-depositing springs (R. Griffiths pers. comm.). As a result of preliminary investigations, a number of questions arose:

1. If the springs were derogated as a result of quarrying, would it be possible to augment the springwater supply and still maintain tufa deposition?
2. In what way could the augmented water supply be introduced to the spring system?
3. In order for tufa to be deposited, are there biological and environmental factors which need to be considered?

1.2 REASONS FOR THE STUDY

In order to answer some of these questions, an understanding of the major processes and influences on tufa deposition in the Mells Valley karst springs was required. This study takes a multidisciplinary approach to the problem by examining and comparing hydrogeological, hydrogeochemical and biological processes taking place within two closely located Mells Valley karst springs and their streams. It had been observed that one of the springs deposited tufa and the other did not (pers. obs.). It was therefore hypothesised that there must be major differences between the two spring systems which influence the deposition or non-deposition of tufa.

The study was initiated to provide knowledge of major contemporary processes taking place in the Mells Valley springs with the aim of determining whether it would be possible to augment the water supply to the tufa spring at Whitehole Farm. This is the first detailed study of the Mells Valley tufa deposits and the work extends existing data and knowledge of Mendip karst hydrogeology and hydrogeochemistry. It also forms a continuation of Part II of the S106 Agreement which requires ongoing hydrochemical monitoring of the Mells Valley springs.

The rationale for the study is as follows:

i. Tufa-depositing springs are individual and unique ecosystems with great scientific and conservation value (Pentecost *et al.*, 2000).
ii. Actively depositing tufa springs have been studied extensively but no detailed research has been carried out on the Mells Valley springs and tufa deposits.
iii. Tufa-depositing springs are protected habitats and may be vulnerable to the effects of water abstractions (Goudie *et al.*, 1993). The threat of derogation of the Mells Valley tufa springs presents a potential problem for Hanson plc. as dewatering at Whatley Quarry is essential for the working of limestone below the water table.

1.3 AIMS AND OBJECTIVES

The main aim of this study was to gain an understanding of major factors which might influence the deposition of tufa at Whitehole Farm Spring. Further to the main aim, this study will determine whether the Whitehole Farm Spring tufa deposits could be maintained by an external, augmented water supply such as Whatley Quarry sump.

In order to achieve these aims, some of the physical, chemical and biological processes taking place at Whitehole Farm Spring were studied and compared with those at St. Dunstan's Well, which is non-tufa depositing. The hydrology and hydrogeology of St. Dunstan's Well has been the subject of previous research, with much of the work having been carried out by the University of Bristol Spelaeological Society and other cave research groups such as the Wessex Cave Club and the Cerberus Spelaeological Society.

St. Dunstan's Well and Whitehole Farm Spring are closely located (2 km apart) within the same geological strata. Both are natural karst springs that have been modified to some extent. The tufa-depositing spring and stream will be considered as a system of environmental processes which take place within a topographical boundary; the water catchment. In this way, it should be possible to highlight differences between the two springs which could have a major influence on the deposition or non-deposition of tufa in their streams.

The components of the system that have been considered in this study are:

1) Geology and hydrogeology. To establish the source and mode of recharge water to Whitehole Farm Spring and compare with that of St. Dunstan's Well.
2) Hydrogeochemistry. To investigate the water chemistry of Whitehole Farm Spring and make comparisons with the water chemistry of St. Dunstan's Well.
3) Environmental biology. To examine and compare the associated biotic and environmental factors at both springs and their influence on the formation, morphology and petrology of tufa deposition.

The objectives of this study were:
i) To make observations on the geology and hydrology of the two study sites and to determine the source and mode of recharge water for Whitehole Farm Spring by carrying out a series of qualitative dye tracing tests.
ii) To record the levels of pH, electrical conductivity, total dissolved solids, air and water temperature, alkalinity, total hardness, calcium, magnesium, sodium, potassium, iron, manganese, nitrate, sulphate, phosphate and chloride for the two study sites for 18 months to determine inter and intra-site differences.
iii) To make observations on algal and cyanophyte ecology and the surrounding vegetation at both sites.
iv) To observe the surface morphologies and inner fabrics of the tufa by sectioning and staining a variety of the tufa samples from Whitehole Farm Spring.

1.4 TUFA

1.4.1 Definition of terms

There is no standard classification for freshwater carbonate deposits (Pentecost & Viles, 1994) and the terms *tufa* and *travertine* have been used interchangeably. In this study, the definitions of tufa by Pentecost (1981) as a soft, porous, calcareous rock formed in springs, waterfalls and lakes in limestone regions and Pedley (1990) as a highly porous or "spongy" freshwater carbonate rich in microphytic and macrophytic growths, leaves and woody tissue will be used to describe the majority of the samples and deposits. The alternative term, travertine, is generally used to describe older, well lithified and often laminated deposits such as those found at Bagni di Tivoli in Italy which have been quarried and used as building stone for over 2000 years (Ford & Pedley, 1996). Travertine can be further separated into two categories on the basis of depositional temperature (Pentecost & Viles, 1994). *Meteogene* deposits are formed mainly in limestone areas with a source of carbon dioxide from the open atmosphere and soil-atmosphere, whereas *thermogene* deposits are more common in areas of volcanic activity. Natural thermal springs that deposit travertine are not common in Britain but two examples can be found at Bath Spa in Somerset and at Matlock Bath in Derbyshire (Pentecost, 1999a).

1.4.2 Processes of tufa deposition

Tufa is a product of an open system in which both matter and energy can be exchanged with the surroundings. This can be simplified as the $CaCO_3 - CO_2$

– H_2O or carbonate (carbonic acid) system. Tufa is one of the crystal forms of calcium carbonate ($CaCO_3$) and is deposited in cool water, mainly as the mineral calcite, by one or a combination of several processes (Glover & Robertson, 2003). It is a calcareous sediment found globally, in many terrestrial, freshwater environments (Ford & Pedley, 1996). Mechanisms for tufa formation are not entirely certain and controversy has always existed over the dominant controlling factors (Pentecost, 1978) but it is now generally accepted that most tufa deposits are the result of the interplay between inorganic and organic processes (Chafetz & Folk, 1984; Ford, 1989).

Tufa deposition can occur as a result of inorganic, physico-chemical processes where emergent groundwater loses carbon dioxide (CO_2) in order to equilibrate with atmospheric partial pressure (pCO_2). Degassing can be increased by hydrological turbulence caused by steep gradients or obstructions within the stream flow (Zeller & Wray, 1956; Jacobson & Usdowski, 1975; Lorah & Herman, 1988). Biological factors, often associated with the presence of certain plant and algal species growing within the stream, enhance the accretion of tufa deposits (Golubic, 1973; Pentecost, 1978; Spiro & Pentecost, 1991). Cyanobacteria readily colonise limestone surfaces and several kinds of algae are associated with tufa and travertine deposits both in the UK and globally (Pentecost, 1990a, 1992; Pentecost & Zhang, 2001). Plants increase the surface area and substrate available for nucleation of the $CaCO_3$ crystals (Emig, 1918; Merz-Preiβ & Riding, 1999). Bryophytes (mosses and liverworts) often form the dominant macrovegetation in tufa streams and are common constituents of tufa deposits (Irion & Müller, 1968;

Pentecost & Lord, 1988; Viles & Goudie, 1990). Drysdale (1999, 2003) reported that aquatic insects, particularly caddis-fly larvae, played a significant part in the rate of travertine deposition by supplying nucleation sites for $CaCO_3$ precipitation on their retreats and food nets.

1.4.3 Tufa morphology and geomorphology

Tufa and travertine deposits are found throughout the world (Ford & Pedley, 1996). Pentecost (1993) reviewed the distribution and formation of 159 active and inactive sites in Britain, mostly dating from the Holocene. Almost half of the sites were associated with Carboniferous Limestone geology such as the tufa cascades at Gordale and Waterfall Beck in Yorkshire and the Lathkill River barrage tufas in Derbyshire. However, active deposition at many of these sites is now minimal (Ford & Pedley, 1996). The largest site, also associated with the Carboniferous Limestone, is at Caerwys in Clwyd, North Wales where an inactive barrage tufa deposit covers an area of 81 hectares. The deposit has been studied in detail by Pedley (1987). A much larger and active barrage tufa system exists at Plitvice National Park in the Dinarid Karst region of Croatia where springs, waterfalls and rivers outflow from the Triassic and Jurassic dolomitic limestone aquifer and become impounded behind actively-accreting tufa dams (Kempe & Emeis, 1985). The photosynthetic activity of plants depleted the CO_2 content of the lakes formed behind the organic barrages and enhanced the deposition of tufa on the dams and marl on the lake beds (Emeis *et al.*, 1987). A series of tufa barrages, pools and cascades in the Brandfontein River in the arid Naukluft Mountains of Namibia were studied by Viles *et al.* (2007). Examination of tufa samples from the actively depositing barrages revealed a fabric comprised of bryophytes (moss) becoming encrusted with tufa in-situ. To the rear of the barrages, dense, laminated tufa deposits of almost pure calcium carbonate (0.1% insoluble residue) were present in an area vegetated by reeds which had also become encrusted in-situ. The results indicated depositional environments influenced by different hydrological regimes of high and low energy and illustrated the wide variety of tufa morphologies to be found. However, the authors found no evidence of aquatic biota (e.g. insect larvae), algal or bacterial associations with the tufa deposits.

The barrage is just one of the many geomorphological classifications and sedimentological terms used to describe tufa deposits. Several different morphological types of tufa have been described by Ford (1989) and Ford & Pedley (1996) and a geomorphological classification for freshwater carbonates has been presented by Viles & Goudie (1990) in which the value of tufa in the present and historical landscape is also defined. In order to identify the many different tufa morphologies, Pedley (1990) suggested a re-defined petrological definition for cool, freshwater tufas in which deposits were classified into two distinct types:

- autochthonous deposits based on the “phytoherm” where deposition of tufa occurs on and around a living, biological framework within the system.
- clastic deposits which form around allochthonous material such as organic debris and inorganic particles.

1.4.4 Karst springs and tufa deposition

Recharge to the water table in a karst limestone aquifer is confined to its catchment limits and is derived from precipitation entering the water table either as "autogenic" (diffuse) recharge or as "allogenic" (point source) recharge which enters the karst outcrop at concentrated points such as sinking streams or swallet holes (Ford & Williams, 1989). These are characteristic features of the karst landscape and form a subterranean link with the discharge point, the karst spring (White, 1988). The springs may or may not deposit tufa. Tufa deposition can take place when spring water becomes supersaturated with calcium hydrogencarbonate ($CaHCO_3$) by the removal of CO_2 from solution. Degassing of CO_2 can be enhanced by water turbulence and increased temperature (Glover & Robertson, 2003). Nucleation of the calcite crystal can take place on a compatible substrate which may be organic or inorganic (Merz-Prieβ & Riding, 1999). Under suitable environmental conditions, tufa can be deposited on the stream bed, flora, fauna and other objects in and around the stream channel and can result in the accretion of diverse, geomorphological deposits such as those found in the UK at Caerwys, North Wales (Pedley, 1987), Nash Brook, South Wales (Viles & Pentecost, 1999) and Slade Brook, Gloucestershire (Pentecost *et al.*, 2000).

1.4.5 The decline in tufa deposition

A decline in tufa deposition in the UK since the late Holocene (c. 2500 BP) has been reported by several authors including Goudie *et al*. (1993) and Griffiths and Pedley (1995) and It has been suggested that the lowering of the water table by the pumping of aquifers could be a contributory factor in the decline. This is a procedure that is commonly carried out by the quarrying industry.

1.5 QUARRYING AND WATER ABSTRACTION

The direct impact of quarries on the environment is recognised (Dept. of Environment, 1991) and the destructive nature of quarrying as a result of soil stripping and removal of grassland and woodland is well known (Gunn & Bailey, 1993), but there are few, if any, detailed studies that focus upon the impacts of water abstractions on natural karst springs and their ecosystems. Low flows in groundwater- dominated streams can arise from a lack of winter rainfall and, although there is no doubt that water abstractions influence the catchment water balance, the impact of low flows and drought in catchments affected by groundwater abstractions is difficult to quantify (Bickerton *et al.*, 1993). Springs are isolated, linear water bodies where longitudinal temperature, water flow and chemical gradients occur and biological species diversity is often low (Giller & Malmqvist, 1999). The intermittent flow of water in temporary or ephemeral springs can create a harsh environment although some flora and fauna can adapt to seasonal drought (Wright & Berrie, 1987).

A large quarry may affect the movement and quality of significant amounts of water both on the surface and underground (Harrison *et al.*, 1992). For example, Fig. 1 illustrates the potential effects of sub-water table quarrying on the water table.

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Fig. 1. The impact of sub-water table quarrying on natural springs in the vicinity of a limestone quarry (after Harrison *et al.*, 1992)

Fig. 1a shows the landscape and the level of the original water table. As quarrying commences, the cone of depression has developed in the water table as a result of quarry dewatering. Some water is discharged to surface streams and some returns to groundwater. The spring is still flowing at this point. In Fig. 1b, a worst-case scenario, deep sub-water table quarrying has caused the level of the water table to drop below the sump and the spring rising, resulting in spring failure and a groundwater flow divide. However, Fig. 1c shows that the situation can be reversed. After quarrying ceases, the quarry void can refill with water, the water table is restored and spring flow resumes.

Water enters a quarry from surface and groundwater sources. A deep and laterally extensive excavation can intercept large volumes of water and inflow must be controlled for safe working of the quarry. Dry working of hard rock quarries is achieved by pumping systems which also have the added capacity to reduce flooding due to heavy rainfall. Dewatering by continuous or intermittent, daily pumping from the quarry sump, which is installed in the lowest level of the quarry is necessary to maintain a dry working area in most large limestone quarries. Pumping water from the sump results in a modification of the groundwater level, known as the “zone or cone of depression” (Fig. 1) and a reduction of water levels in the surrounding aquifer. The greatest drawdown of the water table takes place in the zone adjacent to the excavation and decreases with distance from the workings (Cliff & Smart, 1998).

Due to the complexity of hydrogeological conditions in karst limestones it is often difficult to predict or ascertain the actual effects of water abstractions from quarries (Hobbs & Gunn, 1998). Limestones form heterogenous aquifers (Smart *et al.*, 1991) and the Carboniferous Limestone of the study area, in particular, is composed of numerous, different interbedded rock and clay layers which affect the storage, transmission and flow of water within them. It is also difficult to distinguish between climatic and anthropogenic factors affecting shallow karst aquifers although quarry operators provide the EA with hydrometric monitoring data in order to give a more accurate indication of the impacts of dewatering. However, it is almost impossible to model these effects because of the unpredictable hydraulic properties of karst limestones (Smart, 1994).

1.6 THE STUDY AREA AND FIELD SITES

Whatley Quarry, owned by Hanson plc, is situated on the northern limb of the Mendip anticline and lies within the River Mells surface water catchment at 4 km and 6 km distance to the east from two major karst springs, Whitehole Farm Spring (NGR ST680 480) and St. Dunstan's Well (NGR ST659 479) respectively (Fig. 3). The quarry covers approximately 180 ha of underlying Carboniferous Limestone and is outside the study area. Another smaller quarry covering 60 ha at Halecombe, is situated near the village of Leigh on Mendip (NGR ST690 472) (Fig. 3) and is owned by Tarmac Ltd. Halecombe Quarry (NGR ST698 475) also works the Carboniferous Limestone within the River Mells catchment and is in closer proximity to the springs to the ESE, at approximately 2 km from Whitehole Farm Spring and 4 km from St. Dunstan's Well.

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Fig. 2. Location of the Mendip Hills, Somerset, UK (*not to scale*). (Somerset County Council Tourism Unit)

A third active quarry, the Moon's Hill complex, owned by John Wainwright & Co. Ltd. is located to the west of the study area within the St. Dunstan's Well catchment, 1 km south of the village of Stoke St. Michael (Fig. 3).

The field work for this study was carried out at two sites in the Mendip Hills, Somerset (Fig. 2). The two sites, St. Dunstan's Well and Whitehole Farm Spring, are approximately 2 km apart (Fig. 3)

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Fig. 3. The location of the two study sites (yellow – St.Dunstan's Well, pink – Whitehole Farm Spring). Scale bar = 500 m. Whatley Quarry is located 4 km to the east of Whitehole Farm Spring (*not shown on this sheet*).

The study area is located at the eastern end of the Mendip Hills, on the northern limb of Beacon Hill, the most southerly and easterly of the four Mendip anticlines. The Mendip Hills create a topographic barrier to the prevailing south-westerly winds and precipitation is greater than on the surrounding lowlands known as the Somerset Levels and Moors (Harrison *et al*. 1992). Mean annual rainfall in the central Mendips is approximately 1150 mm (EA data).

1.6.1 Catchment land use

The principal land use in the Whitehole Farm Spring catchment (Fig. 4) is agriculture, predominantly dairy farming on permanent pasture with some extensive beef and sheep enterprises. There are some areas of mixed deciduous and coniferous woodland covering the lower southern slopes of the Mells Valley. The woods form part of the Edford Woods and Meadows Site of Special Scientific Interest (SSSI).

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Fig. 4. Aerial photograph of the Whitehole Farm Spring (pink) location with Leigh on Mendip village to the SE. Scale bar = 500 m. (Hanson plc.)

In the upper catchment, the soils on the slopes of the Devonian Old Red Sandstone are poorly drained surface water gleys and acid brown earths with free-draining calcareous brown earths on the lower Carboniferous Limestone outcrop (Findlay, 1965). During the last five years, however, an increasing area of permanent pasture within the Whitehole Farm Spring catchment has been ploughed and cultivated for the growing of arable crops such as wheat, barley, potatoes and forage maize (pers. obs). The village of Leigh on Mendip

(Fig. 3) has been extended westwards by new housing developments and Halecombe (Fig. 3) and Whatley Quarries to the east have also been extended and deepened during recent years. The St. Dunstan's Well Catchment, also a SSSI, remains largely as permanent pasture for livestock farming (Fig. 5). The village of Stoke St. Michael (NGR ST665 470) (Fig. 3) is central to the area and the two working quarries at Moon's Hill (NGR ST664 460) (Fig. 3) are separated by the valley of the Stoke Lane Stream.

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Fig. 5. Aerial photograph of the St. Dunstan's Well (yellow) location. The village of Stoke St. Michael is to the south. Scale bar = 500 m. (Hanson plc.)

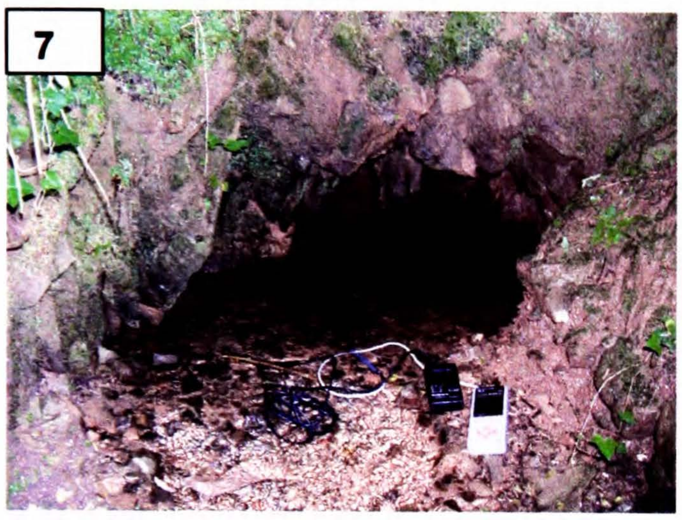
In total, there are seven disused limestone and sandstone quarries in the area, two quarries actively working the andesitic lavas and sandstone (Moon's Hill) on the western boundary and two working the Carboniferous Limestone to the east. As both the catchments are anthropogenically influenced, the karst springs within them are not entirely natural systems.

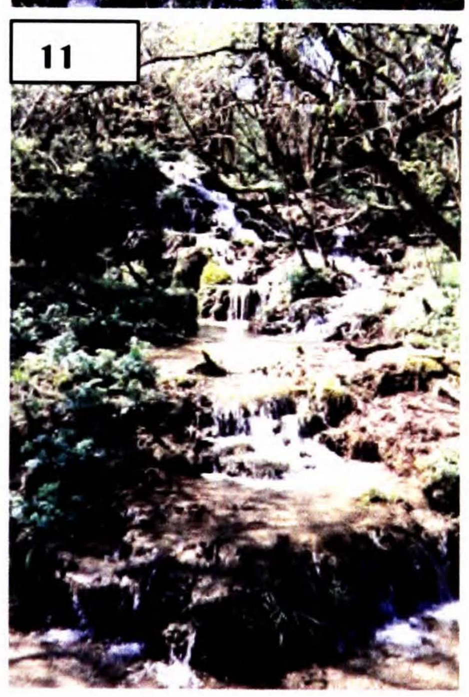
1.7 THE SPRINGS

This study is a comparison of two calcareous springs located in the karst limestone of the Mendip Hills, Somerset one of which actively deposits tufa and one which does not. A karst spring, which formed a surface stream, was selected at each site namely, St. Dunstan's Well, a non tufa-depositing spring and Whitehole Farm Spring, a tufa-depositing spring.

1.7.1 St. Dunstan's Well

St. Dunstan's Well is a large allogenic karst spring resurging at 149 m AOD on the north-facing slope of the Mells Valley. In caving terminology, a resurgence is the appearance of an underground stream fed by a known source such as a sinking stream whereas a rising describes the emergence.of a stream from an unknown source (Ford & Gill, 1979). St. Dunstan's Well consists of two separate springs which emerge at the same elevation and 5m apart. The easterly resurgence was capped by the local water authority for public water supply but the westerly resurgence emerges from a small cave approximately 1 m wide (Fig. 6) known as "Lycopodium Hole" (Barrington and Stanton, 1977). St. Dunstan's Well is the largest allogenic karst spring in the east Mendip Hills (Smith, 1975) and the resurgence is located approximately 300 m NNE of a disused limestone quarry known as Fairy Cave Quarry (NGR ST657 477). A large number of caves and passages were discovered during quarrying, many of which contained exceptional speleothem formations such as stalactites, stalagmites and flowstone (Price, 1977). The site is now controlled by a conservation management group on behalf of the quarry owners (M. Grass, pers. comm.). The natural spring at the westerly rising was studied in this thesis (Fig. 7). It is a perennial and fluctuating stream with a surface feeder stream at Withybrook Slocker (NGR ST655 471) (Atkinson *et al.*, 1967). The stream channel is part natural, part modified as a series of waterfalls, weirs and stone channels had been built in the early 1800s where the stream flows through the grounds of a former mansion, Stoke House, to take the water from the resurgence to the confluence with the River Mells (Athill, 1993). A hydrometric monitoring station used by the Environment Agency is located 20 m downstream. The stream banks are sparsely lined with deciduous trees and ornamental shrubs near the rising with ornamental plantings of yew and laurel approximately 100 m downstream (Fig. 8). There are no tufa deposits at any point within the course of the stream flow.





Risings and sampling points

Fig. 6. St. Dunstan's Well resurging from Lycopodium Hole. **Fig. 7**. St. Dunstan's Well sampling point A. **Fig. 8**. St. Dunstan's Well sampling point B. **Fig. 9**. Whitehole Farm Spring entering the sediment settling tank which had been drained in order to take the photograph. **Fig. 10**. Whitehole Farm Spring emerging at the tank overflow- sampling point A. **Fig. 11**. Whitehole Farm Spring tufa terraces and cascades – sampling point B

1.7.2 Whitehole Farm Spring

Whitehole Farm Spring is the largest of a group of small springs and seepages rising between 140-150 m AOD on the north-facing, wooded slope of the Mells Valley, Somerset. It is a perennial, and constantly fluctuating, karst spring and its stream forms a first order tributary of the River Mells. It has one feeder stream at a sinkhole known locally as Pitten Street Slocker (NGR ST682 472) (Fig. 3) (Barrington & Stanton, 1977). No cave systems have ever been discovered in the locality (W. Stanton pers. comm.). The spring at Whitehole Farm had been used for over a century as a public water supply which was distributed to local villages through a network of underground pipes connected to a large, concrete and brick-built sediment settling tank at the spring resurgence. The approximate dimensions of the settling tank are 2 m high x 2 m wide x 4 m long. It contains some redundant cast-iron fittings and is accessed through a rusting cast-iron inspection cover. The spring itself enters the chamber at floor level through a stoneware pipe approximately 0.3 m in diameter (Fig. 9) and flows vertically upwards to an overflow pipe at the top of the tank. In 1974, a new water main was laid to the village of Coleford (Fig. 3) and the former potable spring supply was abandoned (M Berry, Bristol Water, pers. comm). The stream formed by the overflow (Fig. 10) discharges the water for the tufa deposits which begin to occur at approximately 50 m downstream. A hydrometric monitoring flume is in place approximately 10 m downstream from the settling tank. The rest of the stream channel is natural and meandering and the banks are lined with mainly deciduous trees and shrubs. The tufa cascades and terraces are approximately 100 – 150 m downstream (Fig. 11) and tufa deposition continues through a small area of wetland until the confluence of the stream with the River Mells.

CHAPTER 2.

GEOLOGY AND HYDROGEOLOGY

2.1 INTRODUCTION

The Mendip Hills form a complex series of anticlines consisting of four *en-echelon* periclines or "whaleback" folds, arranged in a WNW-ESE orientation with an average height of 244 m rising to 325 m AOD (Simms, 1995). The periclines are named Black Down, North Hill, Pen Hill and Beacon Hill, respectively. Each of the periclines is steeper on its northern limb than its southern one i.e. assymmetrically folded. Within the cores of the folds are outcrops of Devonian sandstones and older Silurian rocks which rise to 300 m AOD. The geology and geomorphology of the Mendip Hills have been described in detail by many authors including Green & Welch (1965), Donovan (1969) and Ford (1963). The Mendip Hills' strata span the Palaeozoic and Mesozoic Eras and represent approximately 425 million years of Earth history (Simms, 1995). However, the geology of the East Mendip study area is confined to the Palaeozoic Era (428 – 305 Mya).

The East Mendip study area (Fig. 12) lies on the northern limb of Beacon Hill, the most southerly and easterly of the four Mendip periclines. It forms part of a karst landscape of which the main feature is the plateau-like area at 225-255 m AOD underlain by Carboniferous Limestone. The plateau is set below the rising southern slopes of Old Red Sandstone and above the steep, dip-slope valley of the River Mells. The limestone plateau carries no surface streams. The W-E strike-orientated, steep-sided valley of the River Mells is excavated through the Coal Measures at approximately 120 - 125 m AOD. The whole area generally slopes to the north-east and is incised by numerous dry valleys up to 30 m deep, running S-N or SW-NE.

2.2 GEOLOGY OF THE STUDY AREA

The geology of the study area is illustrated in Figs. 12a & 12b.

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Fig. 12a. Geological section (line marked A – B) across the east Mendips illustrating the steep dip angles of the anticline (from Duff *et al.* 1986).

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Fig. 12b. The geology of Beacon Hill showing the location of the two springs in relation to faults and quarries. St. Dunstan's Well lies on the Withybrook Fault. (*Solid black circles show observation boreholes and triangles represent licenced water supply sources*) (from Harrison *et al*. 1992, *not to scale*).

The Beacon Hill study area is part of an east-west orientated, elongated outcrop of Devonian Old Red Sandstone known as as the Portishead Beds (Kellaway & Welch, 1993). The Portishead Beds form the core and summit of Beacon Hill where they rest unconformably on the Silurian pyroclastic rocks. The Silurian rocks of the Wenlock Series are the oldest rocks exposed in the Mendip Hills and were deposited 428 – 421 Mya (Simms, 1995). The rock is actively quarried at Moon's Hill Quarry, Stoke St. Michael (NGR ST 664 460). The rocks are mainly andesitic lavas, coarse tuffs and volcanic conglomerate (Green & Welch, 1965). The non-marine Old Red Sandstone which was deposited approximately 390 – 362 Mya is a non-calcareous, fine grained quartzitic sandstone except for the upper 30 m which can contain a calcareous cement (Green, 1992). It is estimated that the Old Red Sandstone rocks reach a thickness of 456 m in the Beacon Hill pericline where they represent a substantial local aquifer with active recharge and large storage capacity. This is in contrast to the Silurian rocks which are essentially aquicludes with no groundwater flow of any significance within them (Harrison *et al.*, 1992). The Old Red Sandstone rocks are succeeded by the Carboniferous Limestone Series which was deposited between 362 – 333 Mya.

The Carboniferous Limestones and the Coal Measures successively, flank the core of Beacon Hill to the north. In the United Kingdom, the Carboniferous Period is generally divided into two major units, the Lower and Upper Series, both of which outcrop in the study area. The stratigraphy of the Carboniferous Series is summarised in Table 1.

Table 1. Stratigraphy of the Carboniferous Series (modified from Harrison *et al.* (1992).

UNIT	BEDS
Supra-Pennant Measures Upper Coal Series	Coal and clay
Pennant Measures	Sandstones and mudstones
Lower Coal Series	Mudstones
Quartzitic Sandstone Group	Millstone Grit
Hotwells Group	Hotwells Limestone
Clifton Down Group	Clifton Down Limestone unit C
	Clifton Down Limestone unit B
	Clifton Down Limestone unit A
	Burrington Oolite
	Vallis Limestone
Black Rock Group **Carboniferous Limestones**	Black Rock Limestone
Lower Limestone Shale Group	Shales, sandstones and mudstones

2.2.1 The Lower Carboniferous Series

a) The Lower Limestone Shales

This formation lies unconformably on the Upper Old Red Sandstone and is dominated by mudrocks. It represents a gradual transition from non-marine sandstone to typical marine limestones (Simms, 1995). The evaporite shales are fine-grained and thinly laminated mudstones or siltstones with occasional thin limestone beds. The uppermost beds are succeeded by the Black Rock Limestones. The shales themselves are aquicludes and impervious to groundwater circulation and locally are 120-150 m thick (Green, 1992), but groundwater flow can occur in the limestone beds within the shales.

b) The Carboniferous Limestones

The Black Rock Limestone Formation (recognised as two units, Lower and Upper) marks the junction between the impermeable Lower Limestone Shales and the free-draining Carboniferous Limestone. The limestones vary in lithology and Green and Welch (1965) have divided them into three main types: bioclastic limestones, oolitic limestones and calcitic mudstones. The Black Rock Limestone is the main bioclastic limestone in the study area with more than 360 m of strata at Leigh-on-Mendip (Kellaway and Welch, 1993). The beds consist of well-bedded, granular, dark grey to black shelly limestones with a rich fauna of corals and brachiopods. There are abundant chert bands and nodules in the middle part of the Formation, thought to be derived from dissolved and reprecipitated sponge spicules (Simms, 1995).

The Clifton Down Group comprises the Clifton Down Limestone, the Burrington Oolite and the Vallis Limestone, which directly overlie the Black Rock Limestone. The group is characterised by a general absence of crinoidal and fossil debris and consists of dark grey calcite mudstones (chinastones) and crystalline oolitic limestone with some chert bands (Harrison *et al.*, 1992). However, the coral, *Lithostrotion*, can be found at several levels in the Clifton Down Limestone (Simms, 1995). This contrasts strongly with the overlying Hotwells Limestone which comprises the uppermost division of Carboniferous Limestone in the study area. The rocks are massive, pale to mid-grey bioclastic limestones (Kellaway and Welch, 1993) containing abundant corals, brachiopods and other fossils (Simms, 1995). The Hotwells Limestone is exposed at Cook's Wood Quarry (Fig. 12) and at St. Dunstan's Well (Fig. 3).

2.2.2 The Upper Carboniferous Series

The Carboniferous Limestone in the study area is succeeded by the Quartzitic Sandstone (or Millstone Grit) and the Coal Measures which, together, correspond to the Upper Carboniferous Series (321 – 305 Mya). The rocks are mostly non-marine deposits.

The Quartzitic Sandstone Group comprises sandstones, palaeosols and thin coal seams deposited in a non-marine environment (Simms, 1995). The Millstone Grit, a thick-bedded, fine-grained red or grey quartzitic sandstone forms a narrow outcrop approximately 50 m thick at the top of the Hotwells Limestone and the base of the Coal Measures (Harrison *et al.*, 1992). The

Millstone Grit functions as a relatively impermeable bed as do the succeeding Coal Measures (Welch, 1932), which consist of a series of clay beds, shales and coarse red or grey sandstones.

2.3 STRUCTURAL GEOLOGY

None of the beds described in the geological account are horizontal due to the original sequence having been affected by the Caledonian (c. 400 Mya) and Hercynian or Variscan (c. 290 Mya) orogenies. These earth movements during the Palaeozoic Era caused the deformation of the Devonian and Carboniferous rocks in south-west England (Harrison *et al.* 1992) and the severe pressures and uplift resulted in the folding of a series of four *en-echelon* anticlines which became the Mendip Hills.

2.3.1 Faults, bedding planes and joints

Faults are rock fractures resulting from tectonic movements, such as folding, on which relative displacement of the two sides of the break has taken place (Hills, 1963). They are major geological features which can bring beds of different lithology into contact with each other.

Welch (1932) reported the existence of four geological faults within the Beacon Hill study area in his account of the structure of the East Mendips, although one of these, the Stoke Lane Fault, is not marked on later geological maps. Three faults are now shown on the Ordnance Survey 1:10560 Sheet ST64NE. They are, from west to east: the Withybrook Fault (Fig. 12) which runs NNE through the St. Dunstan's Well catchment with a downthrow to the west (Drew, 1968) and the Downhead Fault (Fig. 12) running NNW through the Whitehole Farm Spring catchment with a downthrow to the east. Localised evidence of the Downhead Fault is shown by the slickensiding on joint surfaces at Whitehole Quarry (Duff *et al.*, 1986). This is a process which takes place in a fault plane whereby two surfaces grind against each other to produce grooved or polished surfaces (Ford, 1976). The Downhead Fault was regarded by Welch (1932) as a tear fault radiating into a series of smaller N-S faults. The Soho-Luckington Fault (Fig. 12) runs N-S through the disused Barn Close Quarry (NGR ST97 472) (Fig. 3) located 1300 m to the east of Whitehole Farm Spring with a downthrow to the west (BGS Sheet ST64NE).

Bedding planes and joints play a major part in the development of underground drainage, particularly in the Lower Carboniferous strata of the study area. The distinctive hydrology and landforms of a karst terrain are created by water moving through flow paths determined by bedding planes, joints and fissures in the carbonate rocks (Ford & Cullingford, 1976). Faults and mineral veins may provide conduits for water movement which can penetrate depths well below the drainage basin (Ford, 1976). The hot springs at Bath are believed to be fed by water originating in the Carboniferous Limestone of the Mendip Hills and rising from depths of 2000 to 3000 m (Harrison *et al.*, 1992; Pentecost, 2005). Bedding planes in sedimentary rocks mark a change or interruption in sedimentation and beds are normally horizontal unless deformed by post-depositional earth movements. The Mendip Hills have many examples of the effects of earth movements. In the study area, Palaeozoic tectonic activity has uplifted the original bedding in the Beacon Hill study area to angles of 50° to 80° (BGS sheet ST64NE). Stress fractures can result from compressional forces and folding and this can leave open joints at the top of an anticline that become progressively tighter at lower elevations. The Lower Carboniferous beds dip steeply to angles of 80° to the north as a result of compressional stress from a southerly direction (Simms, 1995). An example of the steep dip angle can be seen in Fig. 13 which shows the exposed Carboniferous Limestone beds at Whitehole Quarry (NGR ST678 479) (Fig. 3), which is located 250 m ESE of Whitehole Farm Spring.

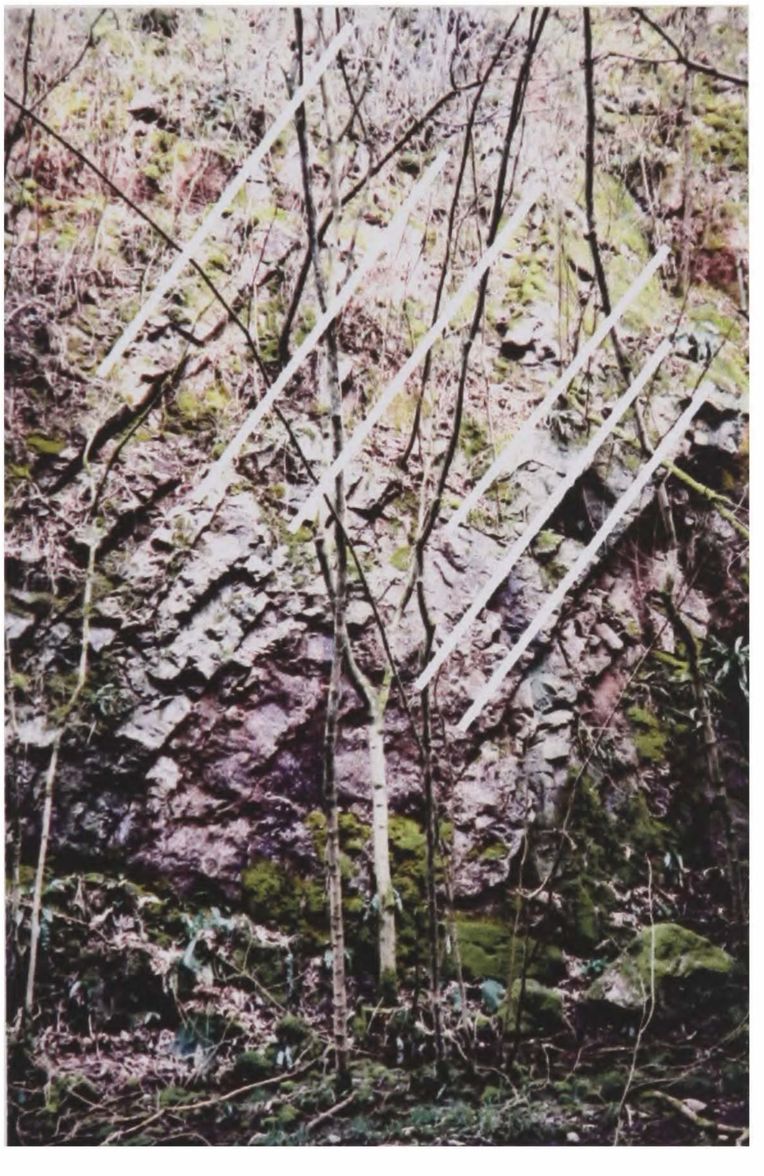

Fig. 13. An example of the folded Carboniferous Limestone beds in the study area. The diagonal white lines indicate the steep angle of dip on the bedding planes (approximately 50°).

2.4 HYDROLOGY AND HYDROGEOLOGY OF THE STUDY AREA

The alternation of permeable and impermeable strata has definable effects on the local hydrology. Water is confined within the Old Red Sandstone aquifer by the impermeable Lower Limestone Shales and the resulting raised water table produces “overflow springs” (Bryan, 1919). These overflow springs form surface streams which flow over the Lower Limestone Shales until they reach the junction of the permeable limestones. At, or around this point, the water sinks underground until it reaches the junction with the impermeable Millstone Grit. The water then resurges from the confines of the Carboniferous Limestone aquifer and again forms surface streams which flow over the impermeable Coal Measures towards the River Mells. In the study area, the existence of dry valleys, sinking streams and sinkholes (or swallets), caves and springs is a characteristic feature of the karst landscape (Fig. 14) and can be classified as “ fluviokarst” (Quinlan, 1988; White, 1988). In order for a rock to be defined as karstifiable it has to possess a higher degree of solubility in natural waters than is found elsewhere (Jennings, 1971). The individual mineral components are dissolved leaving little residual matter and carbonates are the most commonly occurring rocks of high solubility in natural waters. Generally, all rocks containing 50% or more by weight of carbonate minerals are classed as limestones (Gunn, 1986).

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Fig. 14. Subterranean drainage of the Carboniferous Limestone showing some of the karst features seen in the Mendip Hills (from Duff *et al.*, 1986).

2.4.1 The hydrodynamics of groundwater flow in karst limestone

Groundwater normally occupies the voids between the grains in most rocks. These voids are referred to as pores, and the proportion of the total volume of the rock which they occupy is described as the porosity of the rock (Price, 1996). The Carboniferous Limestone is not a porous rock (Drew, 1966), but transmits water through secondary voids such as joints and bedding planes. The secondary voids also control the permeability or hydraulic conductivity i.e. the ease with which water can flow through the rock. As the karst develops, solutionally enlarged secondary voids give rise to the formation of pipe-like conduits and cave passages which control the hydraulic gradient to the outlet at the spring rising (Atkinson *et al.*, 1973). In the Mells Valley study area, the karst limestone rocks slope towards and lie above the River Mells which allows the karst water to drain freely into it under gravity.

2.4.2 The water table

The water table is the boundary between saturated rocks and the overlying strata in which some of the pores are filled with air. It is the surface in an underground water body at which water pressure is exactly equal to atmospheric pressure (Price, 1996). In a highly porous, homogenous geological formation such as sand or gravel, the water table would form a continuous surface from one pore to the next (Davis, 1930; Swinnerton, 1932). The concept of a continuous water table in rock such as the karst limestone is challenged by Drew (1966), who argues that the bulk of flow is through conduits and that hydraulic conductivity is dependent on the position of the limestone within the sequence of geological strata. This can be described as heterogeneous formation where hydraulic conductivity boundaries and gradients exist between different rock units such as shales and mudstones within the limestone aquifer of the study area (see section 2.2). Measurements of the water table are made by assessing the standing water level in observation wells or boreholes drilled to specific angles and depths in the aquifer. In an unconfined aquifer the water table is at atmospheric pressure and consequently where the borehole intersects the water table, it will fill with water until the level in the borehole is the same as that of the immediate water table (Price, 1996).

Water rising from local base level is a more effective indicator of groundwater levels than precipitation percolating downwards through the soil layer to infiltrate the vadose zone. The local base level is the surface water body that gathers and carries away the water from a catchment (Bögli, 1980). In this study, the River Mells represents the local base level. Infiltration of the vadose zone and eventual water table recharge can be affected by many factors in the catchment such as intensity and duration of rainfall, soil type and condition, vegetation, evapotranspiration rates and land use (Davis & DeWiest, 1966).

2.4.3 Groundwater zones

The vadose zone is one of a series of divisions and subdivisions used to categorise an unconfined karst aquifer as shown in Table 2.

Table 2. Karst hydrographic zones (after Davis & DeWeist, 1966; Ford and Williams, 1989)

1 Unsaturated (vadose) zone

- 1a Soil layer
- 1b Subcutaneous (epikarstic) zone
- 1c Free draining percolation zone

Capillary zone

Capillary fringe

2 Intermittently saturated (epiphreatic) zone

Water table

3 Saturated (phreatic) zone

- 3a Shallow phreatic zone
- 3b Deep phreatic zone
- 3c Stagnant phreatic zone

In the vadose zone, the voids and pore spaces may be dry both spatially and temporally. Vadose seepage, which is rain or soil water percolating downwards by gravity, is distinguished from vadose stream flow which describes the flow of groundwater in conduits and passages. Vadose streams respond to recharge in the same way as surface streams (Gunn, 1986). In the capillary zone, water molecules at the water table are subject to upward movement due to the action of surface tension at the air-water interface.

Because of irregular pore sizes in the vadose zone, capillary water does not rise to an even height above the water table, but forms an irregular fringe (Davis & DeWeist, 1966). As water evaporates from the ground surface, it can be replaced by capillary moisture drawn up from the water table and phreatic zone (Fetter, 1988). In the epiphreatic zone, fissures and conduits are intermittently flooded to capacity and the water table rises and falls through this zone. In the phreatic zone, all cavities are permanently full of water. The water table marks its surface and springs occur where the water table intersects the land surface (Jennings, 1985). Water storage can occur in all zones. Groundwater flow in conduits can take place under vadose or phreatic conditions and many vadose streams feed into phreatic conduits before emergence at the surface rising (Gunn, 1986). Gunn (1986) also suggested that storage in phreatic conduits is relatively small and that flow velocities are slower than those in the vadose zone. However, Gunn (1986) argued that flood pulses are transmitted instantaneously by a 'piston' effect which can be described in the following way: water in the saturated zone is displaced under pressure, a rise in the water table follows and a hydrographic response is seen, caused by water being forced through phreatic conduits to the spring rising.

2.4.4 Cave and karst development

The action of meteoric water charged with atmospheric CO_2, penetrating and eroding the bedding planes, joints and fissures of the soluble Carboniferous Limestone leads to the development of a subsurface drainage system. Surface drainage is eventually replaced by active groundwater circulation and the emergence of karst springs containing variable amounts of $CaCO_3$ in solution. Using the Law of Mass Action, three conditions apply to a solution containing a given mineral: i) if there is a net dissolution of the mineral solid, the water can be said to be 'aggressive' or 'undersaturated' with respect to that mineral. ii) if there is a dynamic equilibrium between mineral and solute, the solution is 'saturated.' iii) net precipitation implies that the solution is 'supersaturated' with respect to the mineral. The continual passage of aggressive water through preferential underground routes in the limestone leads to complex patterns of interconnected, solutionally enlarged conduits and often, well developed cave systems (Ford & Williams, 1989). Solution of the limestone is most rapid around stress fractures and lines of weakness in the rock and in folded limestones most caves below the water table are developed along strike joints with passages that are nearly horizontal (Davis, 1960).

Ford & Ewers (1978) differentiate vadose caves into two basic types:
i) the drawdown vadose cave which develops where there is an adjacent non-karstic catchment to supply recharge water to the limestone. The rapid flow through the conduit system produces a drawdown effect in the same way that drawdown is created by pumping the quarry sump. Vadose caves are subject to erosion and the conduit can enlarge rapidly.
ii) invasion vadose caves are created in an already established, open groundwater system. Vertical shafts are formed by further inputs of surface water which enters limestone already being drained by a previous phase of

karst development and in dipping strata, the shafts tend to have a steeper gradient to the phreatic zone than drawdown vadose caves.

The vadose conduit system, as a result of rapid, turbulent flows and often, high clastic and organic sediment loads, is subject to hydraulic erosion and increased surface roughness (Waltham, 1981), particularly if allochthonous material is mineralogically harder than calcite (Smith & Newson, 1974). If the diameter of the conduits exceeds 1 cm, flow becomes turbulent with high flow velocities. The majority of water is transmitted by conduit flow. Diffuse, laminar flow is characteristically slow with long water retention times within the rock (Dreybodt, 1988) and normally occurs along flow paths with smaller cross-sectional dimensions and a high degree of interconnectivity between fissures. In this system, the fissure and fracture network acts as a groundwater storage zone.

Swallet conduits can rapidly transport water to below the water table or to springs, particularly in steeply-dipping rocks (Worthington, 2001) where the major development of cave passages almost always follows the bedding planes (Davis, 1930) and is dominated by the strike of the beds (Jennings, 1985). Ford (1965) described the influence of the steep dip on cave development in the central Mendips. Most sinkholes and conduits form along, or at the intersections of faults, bedding planes and joints (Worthington, 2001) and are important solution features that connect the karst aquifer with the land surface (Stringfield & Legrand, 1971). Vertical shafts, however, are also formed by solution of limestone but are independent of the inclination of the bedding planes (Pohl, 1955; White, 1988). In the Peak District, Ford & Worley (1977) reported that many caves were developed in close association with fault zones and mineral veins. This form of cave development can be seen in the Carboniferous Limestone of the Yorkshire Dales and at Dan yr Ogof, South Wales where the caves coincide with the direction of the dip (Jennings, 1985). However, faults can also act as hydrological barriers and are unfavourable to cave development (Maclay & Small, 1983).

2.4.5 Hydrographs and the characteristics of karst drainage

As karst matures, groundwater movement within it becomes more similar to flow in pipes and channels (Ford & Williams, 1989). Springs fed by a well-developed conduit system respond quickly to rainfall and flood pulses (Jennings, 1971) and the short retention time of water in the rock can be demonstrated by the response to storm events as seen on a discharge hydrograph. A hydrograph is a graphical record of flow volume in litres per second ($l\ s^{-1}$), cubic metres per second ($m^3\ s^{-1}$) or megalitres per day ($ML\ d^{-1}$) plotted against time and usually contains two components i) stormflow, or peakflow and ii) baseflow, which is the steady flow between storm events (Ward & Robinson, 2000). The shape of the hydrograph is an indication of the physical characteristics or response to the hydrological conditions of a catchment. The appearance of the different hydrographs is illustrated hypothetically in Fig. 15. For example, a system dominated by allogenic recharge through a well-developed conduit system has an almost immediate response to storms whereas an aquifer fed by mainly diffuse, percolation water (Fig. 15b) would exhibit a much more subdued response (White, 1988).

Therefore, the response of a karst spring fed by an allogenic system in a mixed lithology basin would display a peaked form, similar to that of a surface stream (Fig. 15a) as opposed to the slow, more smoothed response to diffuse recharge (autogenic) over an entirely limestone basin (Jakucs, 1959; Williams, 1983). Diffuse percolation water passes through the soil layer with a longer residence time and lower flow velocities.

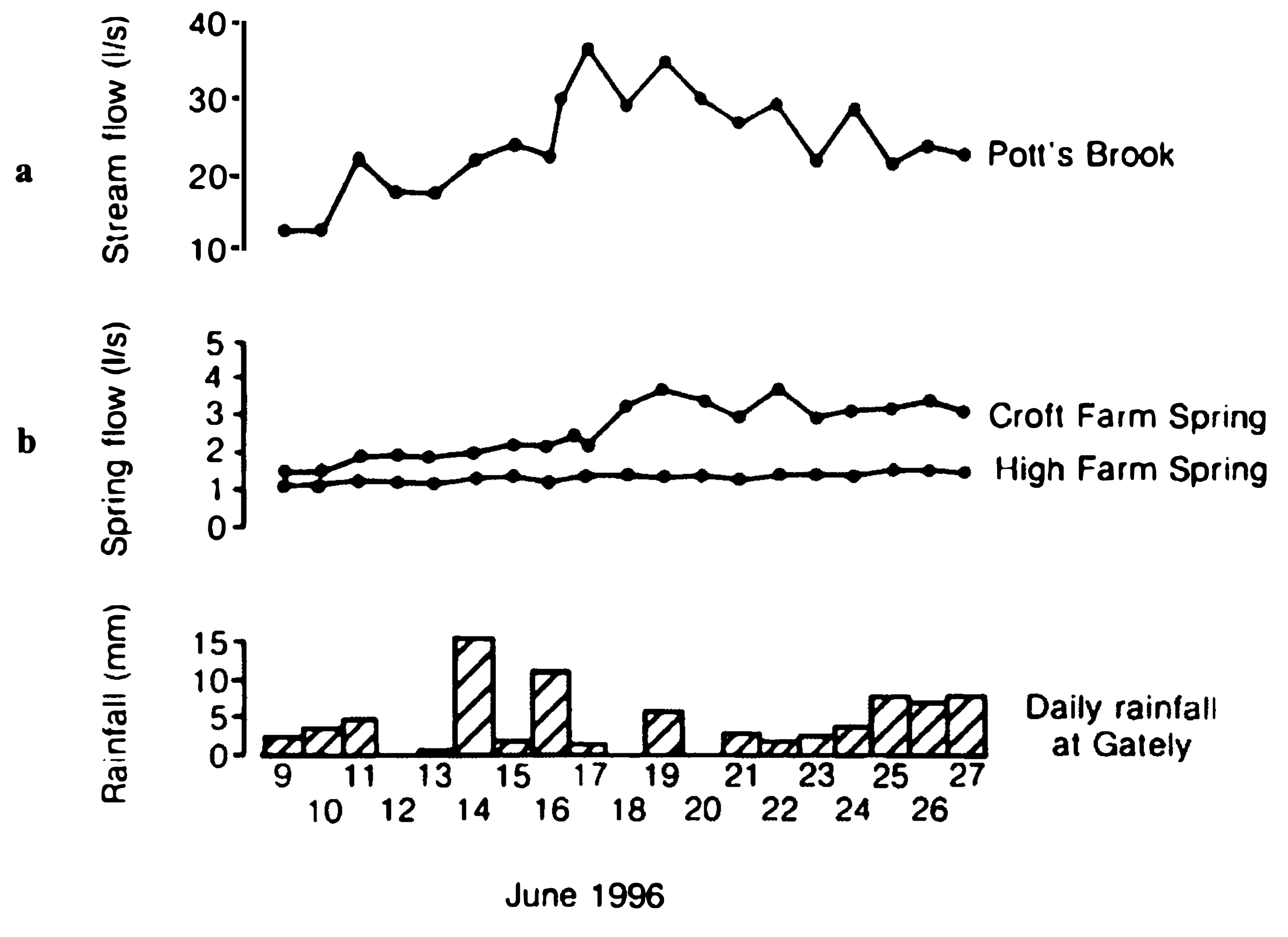


Fig. 15. An example of hydrographs showing the relationship between spring flows and rainfall in a hypothetical catchment. a) shows the response of a surface stream, Pott's Brook. b) shows the different responses of two springs. Croft Farm Spring is fed by a shallow aquifer and High Farm Spring which drains a deeper, percolation-fed aquifer (after Brassington, 1999).

2.5 REVIEW OF MENDIP KARST HYDROGEOLOGY RESEARCH

Karst landscapes are defined by the existence of dry valleys and underground drainage to springs (Ford & Williams, 1989). A karst spring is the natural point of discharge from a karst groundwater system. Groundwater recharge to karst springs occurs in two ways:

i) Infiltration or percolation of water through unconsolidated material or soil to the underlying bedrock. This is described by Drew (1968) as water which does not enter the channel of a surface stream prior to sinking underground. This 'autogenic' (or autochthonous) system is supplied only by meteoric water which diffuses slowly downwards through the soil layer and narrow fissures in the unsaturated zone to the aquifer below.

ii) A karst aquifer fed by an 'allogenic' system derives its water from run-off originating in an adjacent non-karst catchment (Pitty, 1966). In the present study area this catchment is represented by the Old Red Sandstone. Water enters the karst limestone as a surface stream and sinks at a clearly defined point such as a sinkhole or swallet. The water travels underground through discrete fissures or conduits in the rock which can become solutionally enlarged and develop into caves or caverns. Flow through these enlarged channels is often turbulent and rapid in contrast with diffuse flow which is laminar and slow. Both flow patterns can occur simultaneously and the rising where the swallet water emerges at the surface can therefore be described as a 'resurgence' (Newson 1971). Worthington (2001) stated that conduits in carbonate aquifers can exhibit a dendritic network of water channels that feed one or more neighbouring springs. Springs are the discharge points for these groundwater systems and are often located at the junction between rock types of different permeabilities. Fault planes and fracture zones also provide exit routes for groundwater in karst aquifers (Ford & Williams, 1989).

Garrels & Christ (1965) defined two flow mechanisms, diffuse and conduit flow, for the hydrodynamic behaviour of karstic systems, but White (1969) suggested that percolation flow and swallet flow represented a continuum where entirely diffuse flow and entirely conduit flow were end members. Pure diffuse systems and pure conduit flow systems are rare (Smith *et al.* 1976), and Jakucs (1977) noted that many karst systems contained a mixture of both elements with most karst aquifers lying at the conduit end. This view was later supported by the results of karst hydrogeological work carried out in China (Yuan 1981, 1983), which revealed that a three-end member continuum was more appropriate. The concept described fissure flow, diffuse flow and conduit flow as the outer framework for the classification of karst aquifer systems (Atkinson, 1985). However, percolation water can eventually become incorporated within the flow in larger fissures and main conduits at lower points in the hydraulic gradient and the flow paths then combine (Field, 1993). There is much interaction between all components of the karst system.

Much of the pioneering research into the hydrology and hydrogeology of the Mendip Carboniferous Limestone had been carried out by the University of Bristol Geography Department and Spelaeological Society.

The Mendip Karst Hydrology Research Project (MKHRP), Phases I and II (Atkinson *et al.*, 1967) determined the limits of the catchment area for the St Dunstan's Well rising by means of a series of eight water tracing experiments. The time taken for water to travel from the sinkhole at Withybrook to the resurgence was reported to be 6 hrs. During the course of the tests which were carried out between June 1965 and November 1966 the project established a number of hydraulic connections within the present study area including a positive trace from Pitten St. Slocker to Whitehole Farm Spring with a water travel time from sink to resurgence of 4.5 hrs. No additional hydrometric data relating to the water table or rainfall at the time of the tests were published. The full results of the MKHRP, however, determined that there were no hydraulic connections between St. Dunstan's Well and Whitehole Farm Spring. The springs, which were all resurgences, drained two discrete, adjacent groundwater basins within the Carboniferous Limestone aquifer, separated by the Withybrook Fault. As a result of the MKHRP, the eastern boundary of the St. Dunstan's Well catchment was placed between the East End/Bector Wood and Pitten St. valleys and the western boundary placed at Fairy Lane Valley (Fig. 3).

Following the MKHRP, Drew (1968) reported that percolation water contributed the highest proportion of total discharge in an East Mendip study, which included St. Dunstan's Well. 73% of water at the rising was found to be percolation-fed, the remainder being supplied directly via the Stoke Lane Slocker stream. In a study of several Mendip spring risings, Newson (1971)

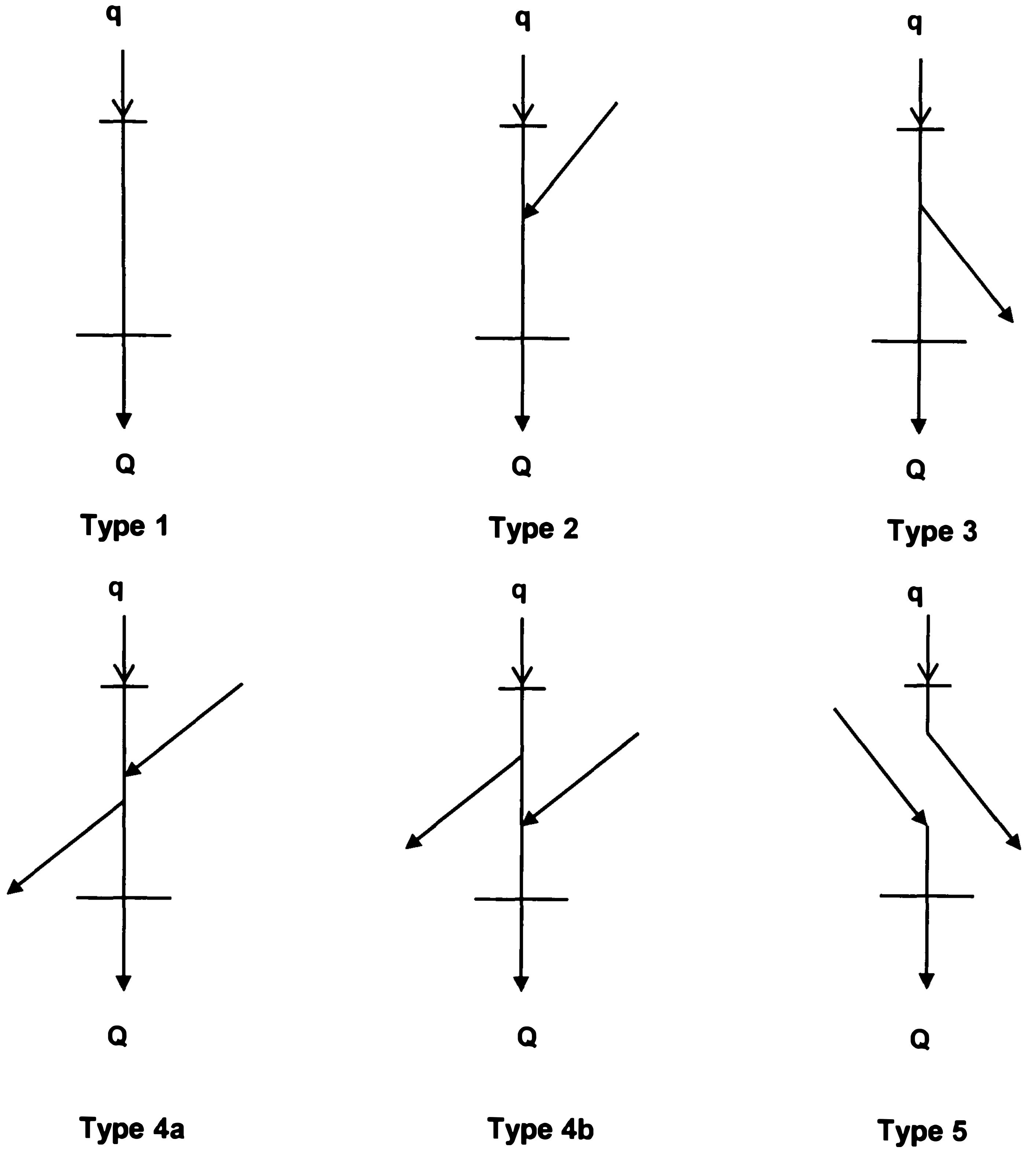


Fig. 16. Potential flow networks from an allogenic karst system. Swallet discharge (q), spring discharge (Q). The diagonal arrows indicate unknown inputs and outputs to and from the system (after Brown & Ford, 1971).

concluded that swallet-fed recharge accounted for 1 - 35% of their total discharge. Atkinson *et al.* (1973) used dye tracing methods combined with stream gauging to deduce flow networks in the East Mendips karst and based their results on five systems previously described by Brown & Ford (1971).

The diagrams in Fig. 16 represent five possible types of underground flow networks in allogenic karst sytems.

Type 1 has a single known input linked to a single known output, Type 2 has additional, unknown input(s), Type 3 has additional, unknown output(s). Type 4a has additional unknown input(s) and output(s) and Type 4b has output from the main conduit before gaining water from a source lower in the system. Type 5 has unknown input which is not connected to the known input. If the volume of water rising at the spring is greater than the recharge at the swallet, other inputs must exist and their volume (Q') is equal to (Q – q). As a result of the tracer tests, Atkinson *et al.* (1973), proposed the existence of a deep phreatic drainage system on the southern flank of Beacon Hill, with karst springs rising at overflow points. For St Dunstan's Well on the northern flank however, a baseflow storage system of flooded fissures was postulated which represented the unknown input to the spring discharge.

In an attempt to measure the different proportions of conduit and diffuse flow in the Carboniferous Limestone of the Mendip Hills, Atkinson (1977b) described the tracing of 61 surface and underground streams using dyed *Lycopodium* spores and individual fluorescent dyes. As a result of the tests he concluded that recharge for the limestone aquifer was an interaction between equal parts of the two components and that karst limestone springs in the Mendip Hills could generally be regarded as conduit springs although most karst springs were recharged by a combination of allogenic and autogenic water. The majority of water storage was within narrow fissures but water transmission was mainly by turbulent flow through solutionally enlarged conduits. Conduits were also found to drain the diffuse component of the aquifer. During the same study, St. Dunstan's Well was shown to consist of many discrete channels where underground flow lines to the two resurgences crossed without mixing.

In a more recent study, Smart *et al.* (1991), used dye tracing techniques to investigate the influence of quarry dewatering on the saturated diffuse zone of the Carboniferous Limestone. The study took place on the southern flank of the Beacon Hill pericline which has the same lithology as the northern flank but has a more shallow dip of 30 - 40° to the south. Several traces were carried out under differing hydrological conditions from several swallets in the vicinity of Torr Quarry (Fig. 12). The results of the tests showed that when the quarry sump water level was low, the consequent increase in hydraulic gradient in the aquifer around the quarry became steeper. This resulted in leakage by diffuse flow from the main conduits. Slower dye travel times than those found in other studies (Atkinson *et al.,* 1967, 1973) suggested a change of function in the karst conduit systems to predominantly diffuse flow. The influence of pumping from the quarry sump on the karst spring systems decreased with distance from the quarry.

2.6 RATIONALE FOR DYE TRACING TESTS

Field observations made prior to the study, revealed that the surface stream that flows into the Pitten St. Slocker originated approximately 2.5 km from the sinkhole at 235 m AOD as an overflow spring rising into a pond at Tadhill (NGR ST672 466) (Fig. 3). The overflow from the pond sinks and then rises again in a field at NGR ST678 465 The stream then flows overland in a north easterly direction in a ditch adjacent to a hedge line and passes into a culvert beneath the Town's End crossroads (NGR ST682 472) (Fig. 3), where there is a small housing development with its own sewage plant. The water then enters the roadside ditch at Pitten St. During periods of heavy rainfall, the Pitten St. ditch holds run-off from the roads and surrounding agricultural fields. The ditch bottom is silty with variable amounts of rock and organic debris from the bank and hedgerow which lines one side of the ditch. The stream then flows through a small, silty, vegetated wetland, the site of the original sinkhole, before entering the "new" sinkhole and the Carboniferous Limestone, which is visible below the 1 m deep soil layer. Field observations made before and during the present study had revealed that at baseflow the surface stream sinks vertically at the entrance to the sinkhole but at stormflow the volume of water in the stream exceeds the drainage capacity of this first entrance (for the purposes of this study called E1) and begins to fill the sinkhole. When the sinkhole capacity is exceeded, the water then overflows into a second passage (for the purposes of this study called E2), which is visible at the back of the sinkhole approximately 2 metres from E1. During prolonged periods of storm flow, the entire sinkhole (E1 + E2) and ditch has been seen to fill and overflow into the wetland and the adjacent field where the overland flow follows the natural north-easterly course of the dry valley towards the disused Barn Close Quarry (NGR ST 693 478) The run-off from storm events ponds up for several hours in the garden of Pitten House before eventually sinking underground (pers. obs.). The Downhead Fault runs NNW-ESE through the garden of Pitten House.

In 1974, following a period of storms and heavy rain, the existing sinkhole at Pitten St. overflowed and more than 500 m of the normally dry valley was flooded causing damage to local properties (W. Stanton, pers. comm.). As a consequence, in 1974, another sinkhole was excavated adjacent to the original and the drainage ditch was diverted to carry the surface water flow from the upper catchment to the new sinkhole as a flood prevention measure (Barrington & Stanton, 1977). Previous hydrogeological research had taken place at the existing, natural sinkhole and the "new" sinkhole had not been investigated in detail until the present study. A series of qualitative dye tracing tests from the new sinkhole was designed in order to determine whether the hydraulic connection to Whitehole Farm Spring had been altered in any way by the excavations. Also, for the purposes of comparison in this study, it was necessary to show if the mode of recharge to Whitehole Farm Spring was similar to that of St. Dunstan's Well, a proven allogenic system.

2.7 GROUNDWATER TRACING

2.7.1 Dye tracing techniques

Dye tracing techniques to determine point to point groundwater connections, i.e. specific recharge to discharge points, have been widely used to trace the subterranean flow to springs in the Mendip Hills (Smart *et al.*, 1991). Results can be obtained by either visual observation of a coloured dye or the use of suitable passive detectors such as activated charcoal or cotton, depending on the chosen method and tracer. Other tracing techniques such as radioactive, bacteriological and chemical methods have been reviewed in detail by Drew & Smith (1969) and Ford & Williams (1989). These methods were not suitable for this project due to the sensitive nature of the spring environment. The dyed spores of the clubmoss *Lycopodium clavatum* have been used very successfully in several qualitative karst water studies, many in the Mendip Hills (Drew *et al.*, 1968; Atkinson *et al.*, 1973; Smart & Smith, 1976). However, the size and high visibility of the plankton nets which need to be fixed at the spring risings for collection of the spores made this method unsuitable for this project. Visually apparent coloured dye plumes would also have been unsatisfactory as they may have caused aesthetic and public relations problems. There was also a risk of missing the dye pulse, especially at night. Passive detection with detectors consisting of activated charcoal or cotton, depending on the tracer used, is generally a more efficient technique (Aley *et al.*, 1989), particularly when the travel time of the dye is unknown. Qualitative tracing with passive detectors is also a cost-efficient technique (Quinlan, 1987).

2.8 AIMS

The aims of this section of the thesis are:

- To determine whether there is a hydraulic connection between the sinking stream at Pitten St. Slocker and the tufa-depositing spring at Whitehole Farm.

- To describe the hydrogeological characteristics of the Whitehole Farm Spring system in the context of the Mells Valley karst.
- To expand the data and knowledge on the karst hydrogeology of the Mendip Hills.

2.9 MATERIALS

The tracer that was used for the series of tests from Pitten St. Slocker was a fluorescent dye "Photine CU", in conjunction with passive detectors made from cotton (described below). Photine CU, is one of a group of fluorescent dyes which absorb light in the ultra-violet wavelengths of the spectrum and is colourless in solution. It is used in the textile and paper industries as an optical brightener to produce a 'blue-white' shade in off-white or unbleached products. It is a 20% solution of urea with ethanolamine and is manufactured by Hickson & Welch Ltd., Yorkshire. Detailed studies of the use of optical brighteners as water tracing agents have been reported by Glover (1972); Smart (1976) and Smart & Laidlaw (1977). Photine CU was used in this study on the basis of the following properties:

- Visibly undetectable to the human eye at relatively high concentrations
- Low biological toxicity
- Rapid photochemical decay on exposure to light
- Binds strongly to unbleached cotton fibres, used as detectors, at low concentrations – minimum detectability 0.36 $\mu g\ l^{-1}$ (Smart 1976; Ford & Williams, 1989).

Dye detectors were made from a set of ten, 20 cm long x 5 cm wide, strips of unbleached cotton material tied at the top with hessian garden string. A 2 g fishing weight was tied with the string to the bottom of the strips to keep the cotton in position. Disposable gloves were worn at all times when handling the dye and detectors to minimise the possibility of contamination. After assembly, the detectors were checked for fluorescence with a long-wave ultraviolet lamp (Black-Ray UVL 56/366 nm) and viewing box (Chromato-Vue CC10). A portable lamp (Mineralight® Model UVGL-48 Multiband UV 255/365 NM) was also used for examining detectors in the field. The detectors were then stored in individual, labelled polythene bags until required.

2.10 METHODS

The ditch and stream channel at Pitten St. were cleaned out in July 2001 using a mechanical excavator to remove large debris from the stream flow and the ditch was then left to settle for 7 days. On the first test day 20 000 l of water from Whatley Quarry sump was pumped from a tanker directly into the sinkhole to flush through any loose sediment which might have collected in the underground fissures. The flushing water had previously been tested as negative for background levels of fluorescence after suspending cotton detectors in the tank for 24 hours before use and inspection under the UV lamp. Optical brighteners, such as Photine CU, are now widely used in household detergents and consequently can be found in domestic waste water. Therefore, background fluorescence levels were determined before the use of the dye in the tests (Ward *et al.*,1998) as an indicator of possible contamination. A detector was suspended in the water entering the slocker and also in the spring chamber at Whitehole Farm and both were left in place for 7 days to determine background levels of fluorescence. On removal, the dye detectors were rinsed in the stream water to remove any loose sediment and examined in the field using the portable lamp. A positive result was indicated if the whole mass of cotton exhibited blue-white fluorescence under UV light (Glover, 1972) rather than a few random specks which were not interpreted as positive results (Mull *et al.,*1988).

The quantity of Photine CU used in the tests was ascertained by means of the following equation:

$\mathbf{W_d = 1.478\ \sqrt{DQ/V}}$ (Aley and Fletcher, 1976)

Where W_d = weight of dye (kg)

D = straight-line distance from injection point to recovery point (km)

Q = discharge at the resurgence ($m^3 s^{-1}$)

V = estimated velocity of groundwater flow ($m\ h^{-1}$)

D = 0.925 km (furthest expected recovery point)

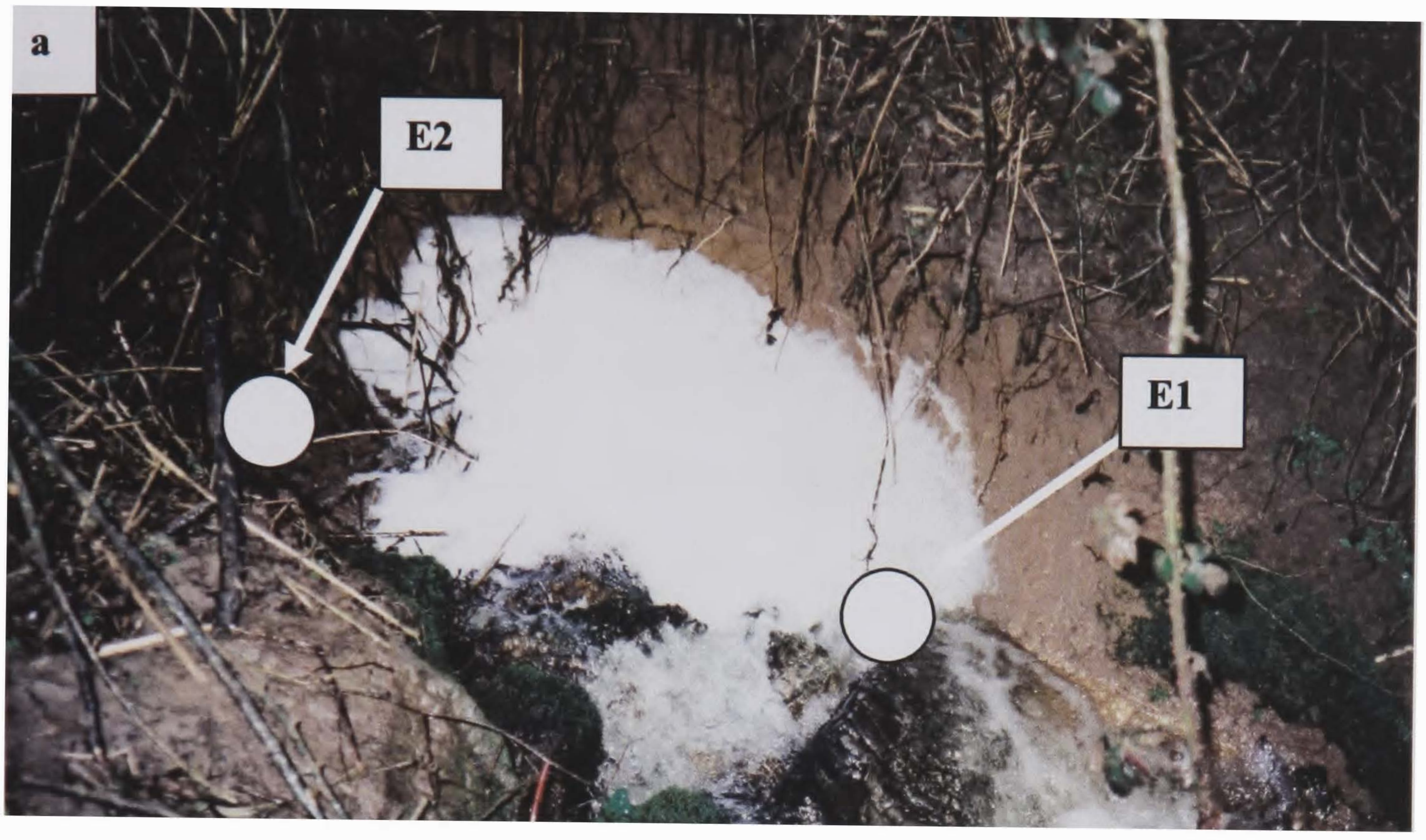
Q = 0.153 $m^3 s^{-1}$ (average for 7 days prior to trace)

V = 0.54 $m\ h^{-1}$ (average water velocity for 7 days prior to trace using velocity meter model : SENSA – RC2)

W_d = 0.8 kg Photine CU

Seven tracer tests were carried out under differing hydrological conditions (for dates, see Table 3), of which, two tests, P1 and P4, were supplemented by using 20 000 l of water pumped from a tanker (tested for fluorescence as previously stated) to simulate the effect of storm flow into the Pitten St. Slocker.

On all test dates, two detectors were suspended in the spring chamber at Whitehole Farm. Dye detectors were also placed at a number of other springs and seepages located within a 500 m radius of Whitehole Farm Spring. In six of the tests (Nos. P1 – P3 and P5 – P7), 800 g of Photine CU was injected into the stream water entering the sinkhole. In one of the tests (No. P4), using the augmented water supply from the tanker, the Photine CU was injected only into the water directly entering the overflow passage (E2) using the tanker hose. No Photine CU entered the first, vertical passage (E1) (Figs. 17a, 17b).



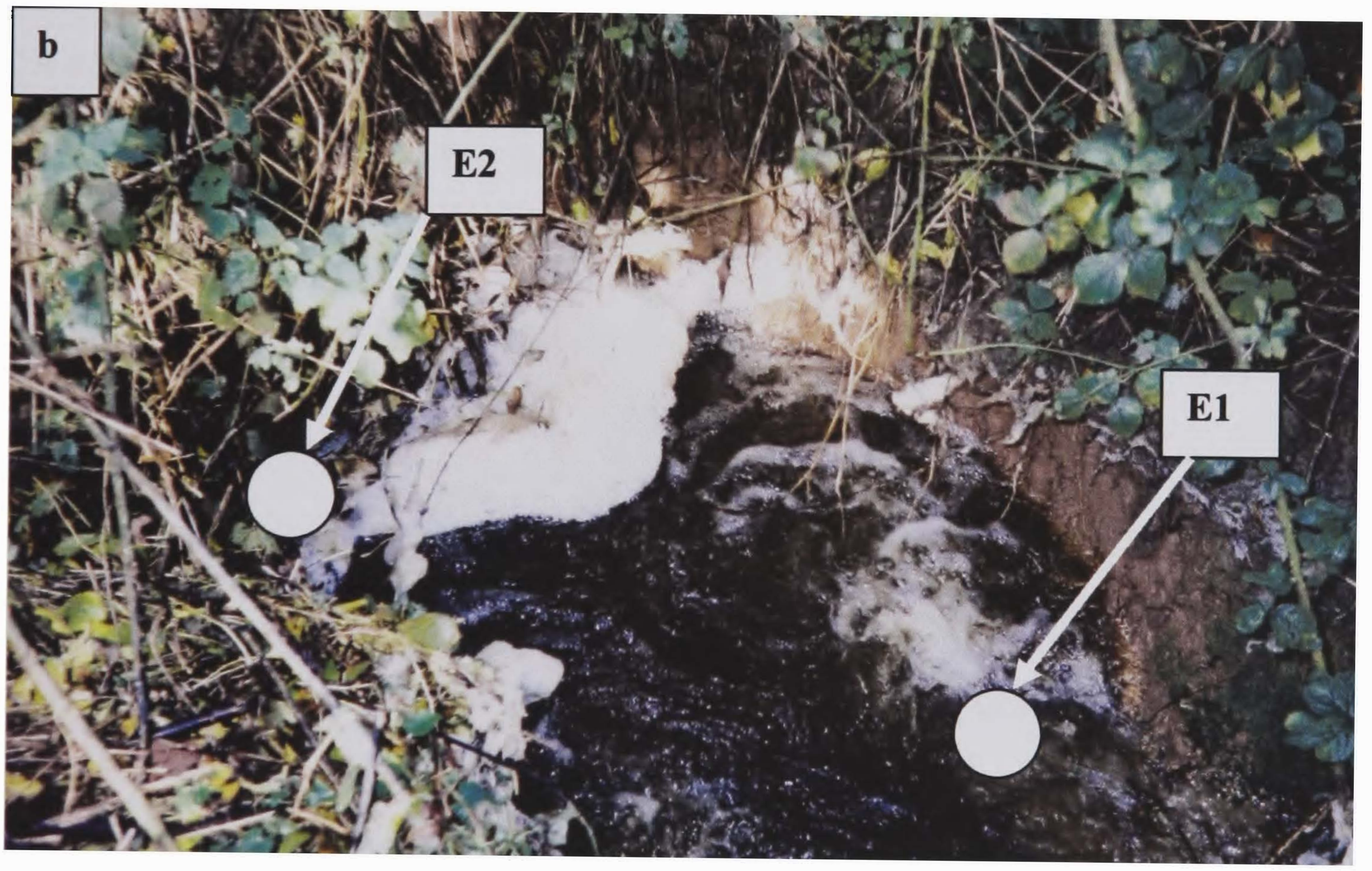


Fig. 17a. Water containing Photine entering the sinkhole at Pitten St. Slocker entry point 1. **Fig. 17b**. Overflow into entry point 2 as the sinkhole begins to fill with water. Distance between E1 and E2 is approximately 2 m.

Table 3. Details of tracer tests from Pitten St. Slocker.

Test No.	Test date	Flow conditions	Injection point
P1.	24 July 2001	Baseflow (augmented)	E1,E2
P2.	27 Aug 2001	Baseflow	E1
P3.	27 Jan 2002	Stormflow	E1,E2
P4.	19 Sept 2002	Baseflow (augmented)	E2
P5.	15 Nov 2002	Stormflow	E1,E2
P6.	02 Dec 2002	Stormflow	E1,E2
P7.	16 July 2003	Baseflow	E1

On each of the test dates, the cotton dye detectors at Whitehole Farm Spring were examined hourly in the field during daylight using the portable lamp, then all detectors were checked daily until a visible result was seen. Positive field results were removed for laboratory examination and replaced with new detectors.

For the purposes of this study, the water table levels were taken from the nearest observation borehole to Whitehole Farm Spring at NGR ST686479 (187 m AOD) approximately 600 m ESE of the spring rising and 800 m NE of Pitten St Slocker. Rainfall and hydrometric data were supplied by the Environment Agency and Entec UK. A series of hydrographs were produced using Microsoft Excel© software to illustrate the relative effects of rainfall, baseflow and stormflow on the local water table, the surface stream at Pitten

St. and the spring resurgences at St. Dunstan's Well and Whitehole Farm. The results were compared with the examples illustrated in Fig. 16. The potential underground flow networks were analysed using the method described by Brown & Ford (1971) (Fig.16).

2.11 RESULTS

The results of the repeated qualitative tracer tests are shown in Table 4. Data were not available from Pitten St. monitoring flume for tests P1 and P2 as it was not installed until October 2001. All tracer tests showed a positive connection between Pitten St. Slocker and Whitehole Farm Spring. Photine was visibly detected at Whitehole Farm Spring and two other locations, under natural conditions (tests P2, P3, P5, P6 and P7) and with artificial recharge (tests P1 and P4) following injection into both entry points (E1 and E2) at Pitten St. Slocker. All tests where Photine was injected into entry point E2 took less than 24 h to arrive at Whitehole Farm Spring. The two tests carried out under natural baseflow conditions of the Pitten St. stream (P2 and P7), where Photine only entered at point E1, took 11 days and 26 days respectively to arrive at the spring resurgence. The local water table was low during these two tests, at 129.3 mAOD and 124.9 m AOD respectively, almost at the local base level of the River Mells at 120 m AOD. Travel times to the spring resurgence were shorter when the water entered passage E2 than when water entered passage E1 only.

Table 4. Details of Whitehole Farm Spring tracer test results and related hydrometric data. PTST = Pitten St. Slocker; WHF = Whitehole Farm Spring; E1, E2 = dye entry points at Pitten St. Slocker; n/a – data not available, m AOD = elevation in metres above Ordnance Datum.

Test no.	Date dd/mm/yy	Swallet entry point for Photine	Previo-us 24hr rainfall (mm)	PTST flow (MLd^{-1})	WHF flow 24hrs later (MLd^{-1})	Water table (m AOD)	Photine travel time to WHF
P1	240701	E1+E2	0	n/a	0.1	135.7	6h
P2	270801	E1	0	n/a	0.1	129.3	264h
P3	270102	E1+E2	28.0	3.6	1.3	147.7	8-24h
P4	190902	E2	0	0.5	0.1	131.4	14-24h
P5	151102	E1+E2	4.1	1.6	2.4	160.9	8-24h
P6	021202	E1+E2	11.6	1.4	2.0	165.6	8-24h
P7	160703	E1	0	0.3	0.1	124.9	624h

Using the data in Table 4, a representation of each of the tracer tests are shown in Fig. 18 in a diagrammatic form based on the flow networks in limestone aquifers (Brown & Ford, 1971; Atkinson *et al.* 1973) as described in section 2.6; Fig. 16.

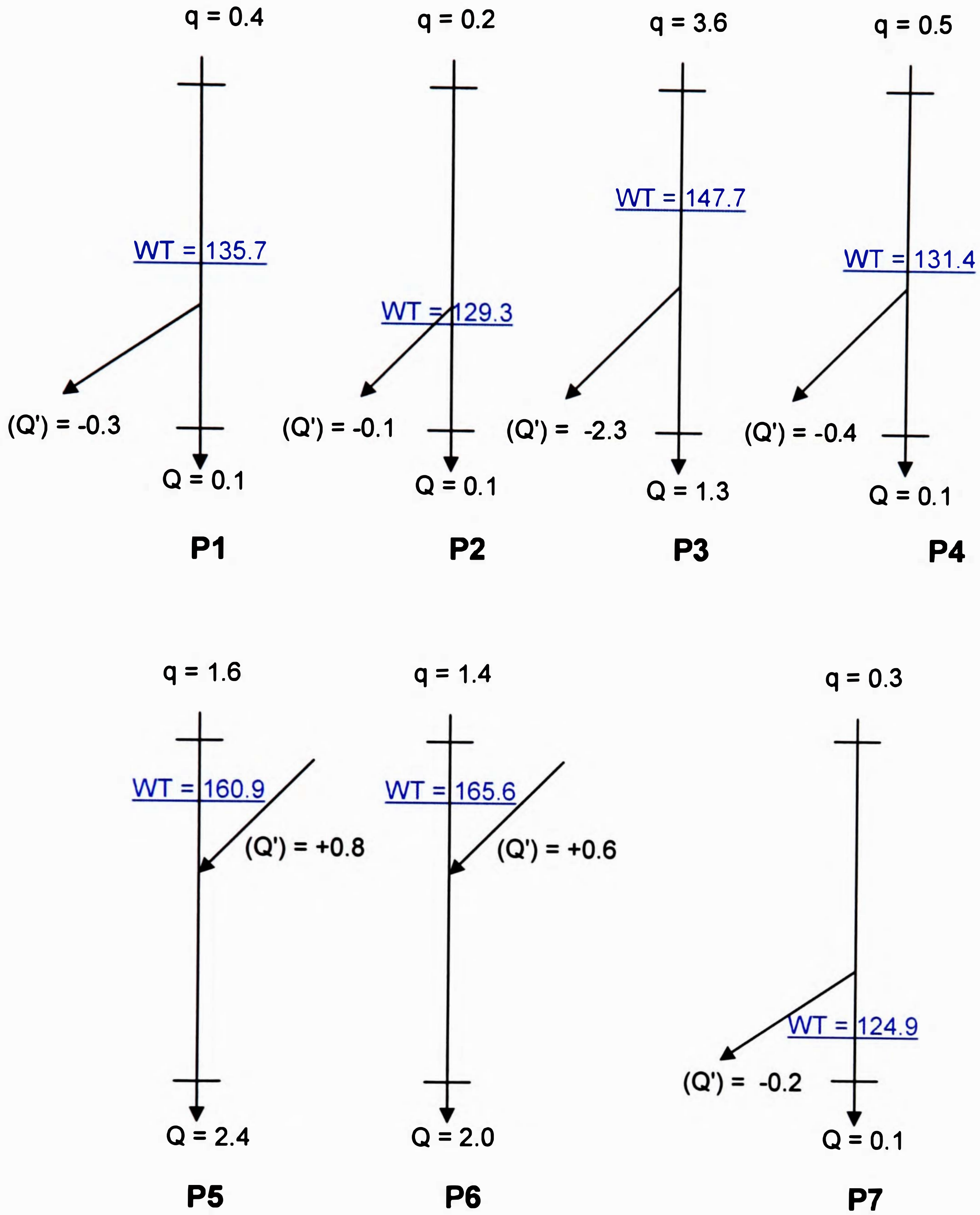


Fig. 18. Diagrams to represent flow networks from Pitten St. Slocker to Whitehole Farm Spring where q = swallet recharge (ML d^{-1}), Q = spring discharge (ML d^{-1}), Q' = (Q – q), WT = height of the water table in m AOD on the day of the test, + or – indicates a gain or loss in total discharge (ML d^{-1}) at Whitehole Farm Spring. For tests P1 and P2, the value of q was estimated as data were not available for those test dates.

It can be seen from the flow diagrams in Fig. 18 that Whitehole Farm Spring exhibited a gain in discharge on tests P5 and P6 (i.e. Type 2, Fig. 16) when the local water table was high (160.9 m AOD and 165.6 m AOD respectively). Neither of these tests received the augmented flow from the tanker but both gained additional water input during stormflow conditions (Table 3). On all other test dates, including P3 also in stormflow conditions, the recorded discharge at Whitehole Farm Spring was less than the recorded recharge from the swallet stream at Pitten St. (i.e. Type 3, Fig. 16). From these results it would appear that the height of the local water table was a determining factor in the increase in volume of discharge at the spring resurgence.

2.11.1 Hydrograph analysis

Fig. 19 shows a series of hydrographs produced from the data to illustrate the different effects of a storm event on 26 January 2002, the day before one of the tracer tests (P3). Using the examples in Fig.15 for comparison, the study area spring hydrographs showed characteristic similarities between c) the surface stream sinking into Pitten St. Slocker and d) St Dunstan's Well rising in their response to rainfall. The first storm event began on 26 January (Fig. 19a) and the response was seen at Pitten St. within 24 hrs (Fig. 19c) and at St. Dunstan's Well within 48 hrs (Fig. 19d). Whitehole Farm Spring e) showed a similar, but less "peaked" response starting on 29 January (Fig. 19e). The smoother form of this hydrograph would be the due to the buffering effects of the settling tank at the rising. The water table (Fig. 19b) fell in the weeks preceding the first storm event and exhibited a gradual rise without falling again before the next storm event whereas c) and d) both fell rapidly and began to rise again on the day of the next storm event on 30 January, a pattern that continued throughout February. Whitehole Farm Spring again showed a similar pattern, with a time lag of 3 days. The decline in spring flow, or baseflow recession, for the three hydrographs is also similarly rapid. The water table remained high for the rest of February. Overall, the hydrographs illustrate that the two springs are dominated by allogenic recharge through a system of conduits and fissures in a shallow aquifer. If the springs had been dominated by diffuse percolation water, i.e autogenic recharge, the hydrographs would have displayed a smoother, slower response to storms.

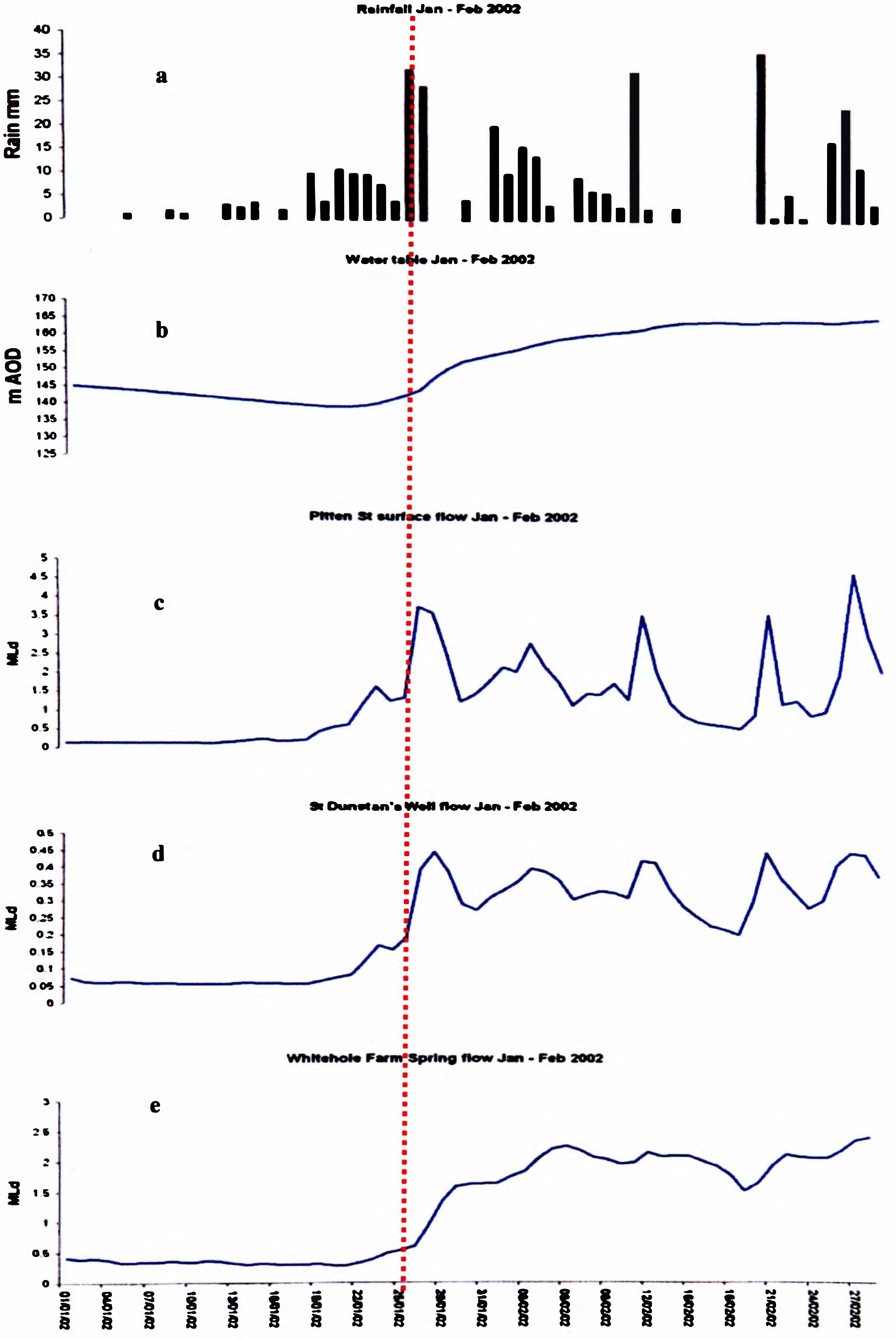


Fig. 19. Hydrographs for 01 January - 28 February 2002 showing a) rainfall b) water table c) Pitten St surface stream flow d) St. Dunstan's Well flow e) Whitehole Farm Spring flow. Red dotted line indicates storm event on 26 January 2002 prior to tracer test P3 on 27 January.

2.12 DISCUSSION

The results of the water tracing tests have demonstrated a positive groundwater connection between the sinkhole, Pitten St. Slocker and the tufa-depositing spring at Whitehole Farm which could be used for the supply of augmentation water to the spring. The sinkhole would appear to contain two discrete channels that converge at or near the spring rising. Water flowing into the first entry point (E1) at the sinkhole travelled the longest distance to the resurgence and water entering the second entry point (E2) took a shorter, more direct route. Water travel times through these channels were dependent on the height of the water table combined with the volume and intensity of rainfall in the Pitten St surface stream and sinkhole. These combined factors also determined the channels by which recharge water enters the groundwater system to Whitehole Farm Spring. The travel times for recharge water from Pitten St Slocker to Whitehole Farm Spring stated in the current study are longer than the 4.5 hrs reported by Atkinson *et al.* (1967) for the MKHRP. The results of the tests in this study have shown the effect of the water table on travel time underground. It would therefore be reasonable to assume that the shorter time reported by Atkinson et al. (1967) was influenced by a higher water table (i.e. > 165.6 m AOD) at the time of their dye-tracing tests in the early 1960s. Unfortunately, there were no details of weather conditions or water table elevations in the report.

A hydrogeological interpretation of the results of the water tracing tests could be seen in the following way: at baseflow, recharge water from the Pitten St.

surface stream was transmitted to the phreatic zone through the sinkhole entry point E1 only (Fig. 17a). The longer travel times from this entry point suggest that the vadose channel at E1 is a vertical shaft (Pohl, 1955; White, 1988) to the water table which has formed by solution of the limestone, independently of the Carboniferous Limestone bedding planes and joints and in relation to a lowering of the water table. The constant baseflow of water into this conduit from the Pitten St. stream ensures recharge to Whitehole Farm Spring by continuous displacement of water from the main phreatic conduit below the water table to the spring rising when the hydraulic gradient and pressure is low. Water entry point E2 at the sinkhole (Fig. 17b) is active only when the volume of water in the stream exceeds the transmission capacity of E1. The conduit would follow the dip and strike of the bedding planes and joints and could represent a former phreatic conduit from a stage in earlier downcutting of the River Mells. This would provide an explanation for the calculated flow diagrams in Fig. 18 which categorised the Whitehole Farm Spring system as a Type 2 – additional, unknown input (tests P5 and P6) or Type 3 – additional, unknown output (tests P1, P2, P3, P4 and P7) using the criteria set by Brown & Ford (1971) and Atkinson *et al.* (1973). The results of tracer tests P5 and P6 in Fig. 18 indicated a Type 2 response, ie. gaining water from an unknown source.

In view of the storm conditions prior to these two tests it is suggested that the additional input, in this instance, was a combination of diffuse recharge provided by rainfall and leakage of groundwater through the wider catchment. Therefore, E2 would be a periodically active sink which functioned only when the first sink and channel at E1 was completely full. Following a storm, part of the channel from E2 could hold ponded water and become a permanent water trap within the vadose conduit. The ponded water would represent a storage reservoir which was activated only when the water table rose to that level. The contribution of the stored water would then increase output above the measured input. The two conduits did not converge but reached the water table at separate points to resurge at the same point. When the water table was below the critical level the flow network would become a Type 3. The conduit development would appear to be that of a drawdown vadose cave system as defined by Ford & Ewers (1978) with phreatic and water table sections as suggested by Ford & Williams (1989). The subterranean flow route did not mirror the surface topography as would be expected, but instead, the water was intercepted and guided by the Downhead Fault to rise at Whitehole Farm Spring instead of following the natural course of the dry valley to the north-east. The karst stream system runs north-west along the strike of the strata and almost at right angles to the surface drainage, i.e the dry valley, which runs north-east (Fig. 20). The stream is then resurgent at the junction with the Millstone Grit and Coal Measures (Fig. 13).

The hydrographs demonstrated that the flow at both springs was dominated by allogenic recharge water (Figs 19d, 19e). The hydrograph for Whitehole Farm Spring (Fig. 19e) displayed a more smooth form than the surface stream (Pitten St.) or the well developed karst spring (St. Dunstan's Well). However, the settling tank at the spring rising, which contained a constant volume of approximately 16 m^3 of water, would have acted as a buffer to the effects of stormflow and should not be interpreted as the response of diffuse recharge to the spring (Jackucs, 1959; Williams, 1983).

In conclusion, the data collected in this section of the study have revealed that:

1. There is a hydraulic connection between the sinking stream at Pitten St. Slocker and Whitehole Farm Spring which is guided by the Downhead Fault..
2. Augmentation water could be introduced to the Whitehole Farm Spring system via the ditch and sinkhole at Pitten St.
3. The sinkhole has two discrete channels to the water table.
4. Travel time of recharge water to the spring is influenced by the height of the water table.
5. Whitehole Farm Spring drains a shallow karst aquifer.
6. A large proportion of recharge water to Whitehole Farm Spring is allogenic from the upper Old Red Sandstone catchment.
7. In the context of the Mells Valley karst, the Whitehole Farm Spring system is still developing and is similar to, but less mature than, the St. Dunstan's Well karst system which is 2 km upstream. The main underground conduit from Pitten St. Slocker to Whitehole Farm Spring is not yet capable of containing all the flow from the catchment. Nevertheless, the findings demonstrate that the Whitehole Farm Spring system is hydrogeologically similar to the St. Dunstan's Well system.

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Fig. 20. Conceptual routes of subterranean water flow from Pitten St. Slocker to Whitehole Farm Spring illustrating the influence of the Downhead Fault on the diversion of water from the natural dry valley. Scale – 1 cm:100 m

CHAPTER 3 – HYDROGEOCHEMISTRY

3.1 HYDROGEOCHEMICAL PROCESSES

Groundwater acquires its chemical composition as a result of processes such as mineral dissolution and precipitation, oxidation and reduction, ion exchange, biological respiration and decomposition taking place within the catchment (Matthess, 1982). When precipitation, falling as rain or snow, enters the soil, the most important natural process is the dissolution of carbon dioxide from the soil atmosphere where organisms also consume large amounts of dissolved oxygen from atmospheric water (Price, 1996). Low concentrations of sodium, chloride and sulphate can also be present in precipitation, derived from seawater spray in the atmosphere (Lloyd & Heathcote, 1985). As recharge water flows through and eventually out of the aquifer, it assumes a chemical character as it interacts with the soil zone and different geological facies (Fetter, 1988). Precipitation which infiltrates soluble carbonate rocks such as limestone and dolomite, develops relatively rapidly into calcium or calcium/magnesium bicarbonate-type groundwaters which may also contain varying quantities of other ions depending on the composition of the aquifer (Hounslow, 1995). Human activities such as agriculture, urbanisation and industry can also influence the composition of groundwater by raising levels of organic and inorganic pollutants (Hem, 1989). Groundwater in well-developed karst terrains, in particular, can be vulnerable to contamination because of the large solutional openings, or conduits, which allow rapid transport of pollutants to the aquifer (Quinlan, 1988).

3.2 THE SYSTEM CONCEPT

The karst springs examined in this study can be seen as a structured series of units, or individual components, functioning as an environmental system. White *et al.* (1984) suggested that all natural systems have the following common characteristics:

- They have some structure or organisation
- They all function in some way
- There are functional as well as structural relationships between the units
- Function implies the flow and transfer of some material
- Function requires the presence of some driving force, or source of energy
- All systems show some degree of integration of units.

Environmental systems can be described as thermodynamic or energy systems which are confined within defined natural or man-made boundaries (White *et al.*, 1984). They can be classified into three fundamental categories in relation to the behaviour of the system boundary with its surroundings (Fig. 21). In (i) an isolated system, there is no interaction with the surroundings across the boundary. (ii) Closed systems only allow the transfer of energy with their surroundings (described by Ford & Williams (1989) as a two-phase system). (iii) Open systems allow the transfer of both matter and energy across the boundary and, in the context of this study, refers to a body of water where all three phases, solid, liquid and gas, are able to react together (Stumm & Morgan, 1996)).

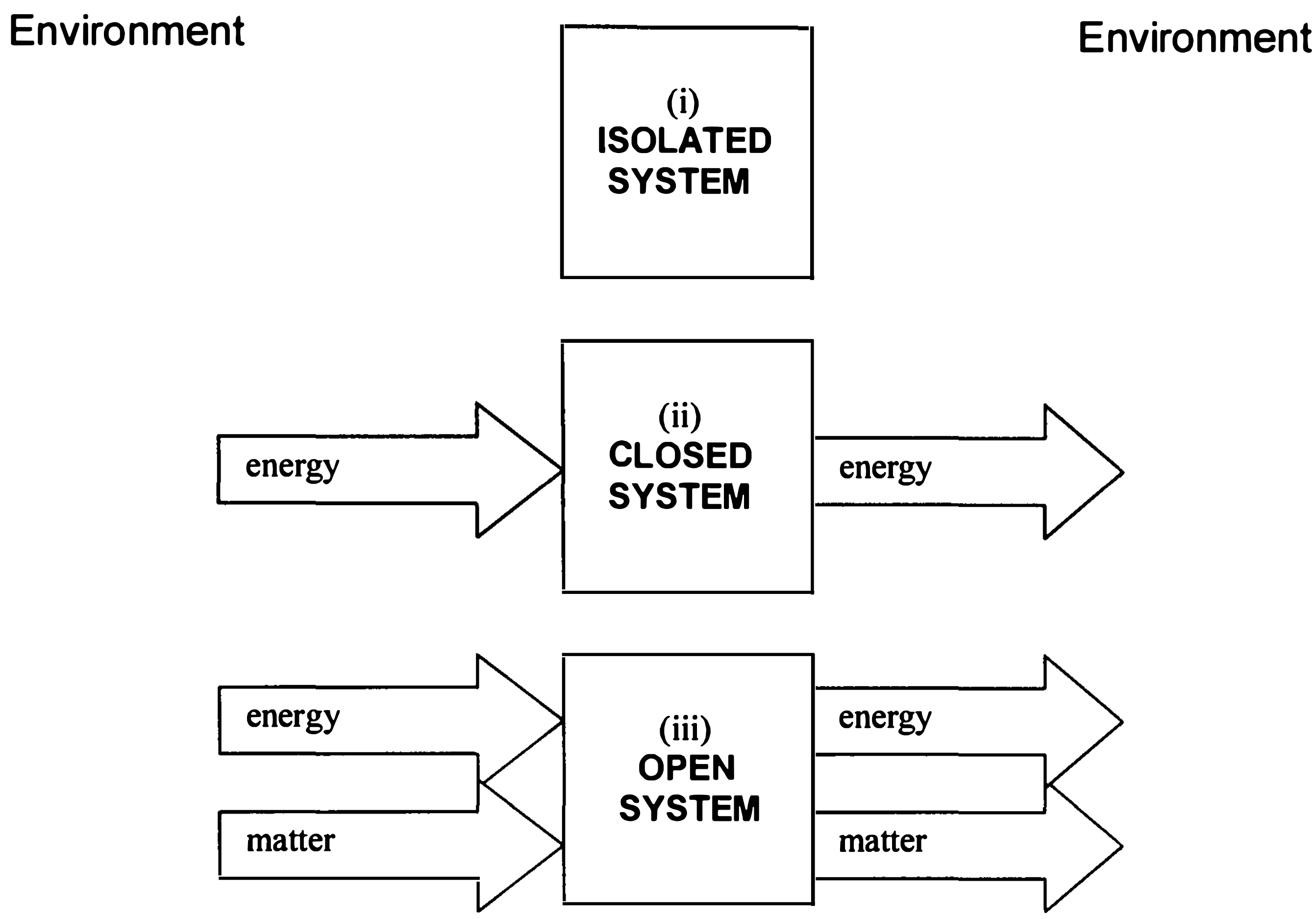


Fig. 21. Three types of system showing the interaction with their surroundings across the system boundaries (after White *et al.*, 1984; Stumm & Morgan, 1996).

If the diagram in Fig. 21 is applied to a cave system in karst limestone, such as Fairy Cave Quarry (Chapter 1, Section 1.7.1), in its simplest form, energy is supplied by the flow of subterranean water and matter is supplied by water, atmospheric and dissolved CO_2 and calcite ($CaCO_3$).

3.3 EQUILIBRIUM

Chemical equilibrium within a natural closed system such as a phreatic karst fissure would mean that, as calcium carbonate dissolved, the solute concentration would gradually increase over time until it reached a point when solute ions were moving from the solid to the liquid at a rate equal to the reverse process (Ford & Williams, 1989). However, dynamic functioning systems, such as those found in the natural environment, are open systems in which both matter and energy can cross the boundaries and be exchanged with the surroundings. An environmental system must maintain a state of structural organisation and self-regulation whilst these exchanges are taking place. These are known as equilibrium states and the system through which energy and matter constantly flow tends to evolve into a characteristic equilibrium termed a steady state (Stumm & Morgan, 1996). True equilibrium states require an isolated or closed system and only occur when no reactions are proceeding. They rarely occur in the natural world. True equilibrium could be defined as static equilibrium in which opposing processes completely stop, rather than cancel each other out. Anderson (1996) described this as the lowest energy state to which the system will try to return after being disturbed. He further stated that natural water systems obtain their equilibrium through a variety of chemical, physicochemical and biological processes taking place within them which constantly change between stable and metastable states. These processes involve energy and mass changes/transfers within the water body. This is applicable to the carbonate system where the mass transport of the dissolved ions Ca^{2+}, HCO_3^- and CO_3^{2-} takes place from the mineral surface to the solution and aggressive species H_2CO_3 and H^+ transfer from the solution to the mineral surface (Dreybodt, 1988). This interaction can be described as a state of dynamic equilibrium. Dynamic equilibrium occurs when opposing forces or processes continue to operate but cancel out amongst themselves. It is a state of continued but balanced change (White *et al.* 1984). The behaviour of a chemical system at equilibrium is described by Le Chatelier's principle (Lloyd & Heathcote, 1985) which states that a change in any of the factors that determine the equilibrium conditions of a system, i.e. concentration, temperature or pressure, will cause the system to change in a direction that will minimise the effect of that change. For example, if a solution becomes more concentrated, the equilibrium will shift in order to reduce its concentration (Baird, 1999).

3.4 CALCITE

Calcite is the most common mineral form of calcium carbonate ($CaCO_3$) found in carbonate rocks and it has a rhombohedral crystal structure (Berry & Mason, 1959). Sparite, or sparry calcite, refers to crystals of 5 µm or more in diameter and micrite, or microcrystalline calcite, describes grains of < 5 µm in diameter (Adams *et al.*, 1984). Calcite is the thermodynamically stable polymorph of calcium carbonate, which has at least three polymorphic forms in nature; calcite, aragonite and vaterite (Tucker & Wright, 2001). Aragonite has an orthorhombic crystal structure and is less stable, but freqently occurs in caves. Vaterite, with a hexagonal crystal structure, is rare and much less stable. It is transformed to calcite or aragonite very rapidly in the presence of water (Picknett *et al.* 1976). However, the presence of vaterite has been identified by X-ray diffraction as a co-precipitate with calcite in stream sediments in the Sichuan Province, China (Lu *et al.* 2000). The chemical composition and crystal structure of dolomite ($CaMg(CO_3)_2$) is similar to that of calcite (White, 1988). However, the Carboniferous Limestone rocks in the East Mendip study area are classified as very high purity limestone, often containing >98.5% $CaCO_3$ as calcite (Harrison *et al.*, 1992) and, as such, contain only minor amounts of dolomite.

A number of techniques have been used to study the kinetics of calcite crystal growth which include the preparation of supersaturated solutions, observation of the onset of the crystal form and changes in the concentration of the solution (Nancollas & Purdie, 1964; Nancollas & Reddy, 1971; Reddy & Nancollas, 1971). The results of these studies showed that the formation of crystals from solution takes place in two steps; first, nucleation – the formation of a calcite seed crystal and second, the growth of the crystals by deposition of the mineral on the nuclei or seed crystals. Nucleation is the formation of a solid phase from solution and can be:

- homogeneous – forming in the bulk of the solution
- heterogeneous – forming in contact with another particle or surface

Under experimental conditions in the laboratory, nucleation was reported to have taken place on the walls of the reaction vessel (House, 1981) or on dust particles in suspension (Reddy,1983). A lack of suitable nucleation sites can inhibit calcite crystallisation in natural aquatic systems (Suarez, 1983).

3.5 SATURATION STATES AND THE LANGELIER INDEX

Using the Law of Mass Action, Ford & Williams (1989) described a solution containing a given mineral to be in one of the following three conditions with respect to the given mineral solid phase:

i. The forward reaction proceeds and there is net dissolution of the mineral. The solution is described as 'undersaturated' or 'aggressive' with respect to the mineral.

ii. There is a dynamic equilibrium where the products are continually being formed at the same rate as they are decomposed. The solution is 'saturated' with that mineral.

iii. The back reaction predominates leading to net precipitation of the mineral. The solution is now described as 'supersaturated'.

The dissolution of calcite proceeds in relation to the acidity of the water and is usually indicated by pH levels below 6.5 (Stumm & Morgan, 1996). The water in this state is described as "aggressive" to calcite (Trudgill, 1985). The disequilibrium between the mineral phase and the solution is expressed as the saturation state. It is the saturation state with respect to calcite, i.e. the amount of surplus $CaCO_3$ in solution, which determines the potential of the water to precipitate calcite (or tufa). By investigating how far the solution is from equilibrium, by hydrogeochemical analysis, it is possible to determine the reactions that are taking place as water is moving through a system (Stumm & Morgan, 1996). Most karst waters are not in equilibrium with solid calcite. Many are undersaturated and aggressive and some are supersaturated and capable of depositing speleothems or tufa (White, 1988). The calculated Saturation Index (SI) is a means of quantitatively determining the deviation of carbonate waters from equilibrium (Langmuir, 1971). The SI can also be referred to as the "Langelier Index" which is, specifically, the calcium carbonate saturation index (Hounslow, 1995). In any solution where the concentration of dissolved ions is known, their product can be calculated as the ion activity product (IAP). The sum of these ions is equal to the solubility of the mineral, known as the solubility product (K_{sat}). Hounslow (1995) further explained that the IAP is compared to the solubility product of the particular mineral - which in this study is calcite - in the form of the logarithm of the ratio. The log of the IAP divided by the K_{sat} is known as the Saturation Index (SI). This can be expressed by the following equation:

$$\text{Saturation Index (SI)} = \log (IAP/K_{sat})$$

If the SI equals zero, i.e. $IAP = K_{sat}$ then the water is at equilibrium with the mineral phase, a negative SI indicates undersaturation and a positive value for the SI indicates that the solution is supersaturated with respect to the particular mineral and the reaction should proceed in the direction that will precipitate more solid (Hem 1989). As the scale is logarithmic, the degrees of saturation vary by the order of magnitude of ten, therefore, in the case of calcite solubility, a $SI_{calcite}$ value of 0 corresponds to equilibrium while values of +1 and –1 correspond to 10 times and one tenth saturation respectively. When calcite is in equilibrium with water, the solubility product of the Ca^{2+} and CO_3^{2-} ions in solution is expressed by their product $[Ca^{2+}][CO_3^{2-}] = K_c$. In this case, the SI for calcite (SIc) can be expressed in an alternative way, i.e. the pH of the solution minus the pH at which calcite precipitates. In this form the SIc is known as the Langelier Index (Hounslow, 1995, Mathess, 1982). This can now be written as:

$$\text{Langelier Index} = SI_{(calcite)} = pH_{actual} - pH_{saturated}$$

If the calculated Langelier Index is positive, the solution is supersaturated and if it is negative the solution is undersaturated with respect to calcite. An alternative form of index used by some workers is the saturation ratio (SR) or (Ω). This is a non-logarithmic version of the SI, where equilibrium is reported as 1.0 (Ford & Williams, 1989).

Supersaturated solutions can be labile (i.e. spontaneously precipitate through nucleation directly from solution) or metastable (i.e. yield no precipitate). The metastable concentration range can vary greatly with critical concentrations above which spontaneous precipitation can occur, being as much as ten times the solubility value (Reddy, 1983). Drever (1997), stated that an energy barrier must be surmounted before homogeneous nucleation can occur, even in a supersaturated solution, i.e. one having a Saturation Index >0 (Reddy, 1983). A certain critical degree of supersaturation must occur before the formation of stable nuclei can take place (Berner, 1980). Homogeneous nucleation is rare in karst studies (Ford & Williams, 1989). At low saturation levels, nucleation can only take place heterogeneously in contact with another solid phase, ideally one with a compatible atomic structure. In natural waters, heterogeneous nucleation is the predominant formation process for crystals (Stumm & Morgan, 1996). Foreign particles however, can also inhibit crystal formation. Picknett (1964) and Reddy (1975,1983) cite both magnesium and phosphate ions as kinetic inhibitors of calcium carbonate mineral formation. Under laboratory conditions, Nancollas & Reddy (1971) demonstrated that calcite formation could be inhibited by the presence of phosphate (PO_4^{3-}) when the solution was near to equilibrium. Calcite crystal growth was found to be impeded by adsorption of the phosphate molecules at the calcite crystal growth surface. Magnesium ions in solution were also found to decrease the rate of calcite crystallisation by becoming incorporated in the original calcite seed surfaces and developing a magnesium surface which grew at a slower rate (Picknett, 1964). The slower growing faces dominated the morphology of the crystals causing the calcite crystal form to change. Similar morphological changes as the result of the presence of Mg^{2+} in solution have been reported by Zhang & Dawe (2000).

3.6 CARBONATE CHEMISTRY AND KINETICS

The process of calcite dissolution can be summarised by the following sequence of chemical reactions which are based on the concept of equilibria in solution. In pure water, the solubility of calcium carbonate is low, 15 mg $CaCO_3$ per litre at 20° C (Mathess, 1982). $CaCO_3$ dissociates into a metal cation (Ca^{2+}) and anion (CO_3^{2-}) during the process of dissolution:

$$CaCO_3 \xrightarrow[\text{dissociation}]{} Ca^{2+} + CO_3^{2-}$$

The solubility of $CaCO_3$ decreases with temperature rise but increases in the presence of free carbon dioxide (CO_2). When CO_2 gas is brought into contact with pure water (H_2O), CO_2 dissolves until equilibrium is reached. At this point, using Henry's Law, the concentration of dissolved CO_2 gas is proportional to the partial pressure of CO_2 in the gas phase:

$$CO_{2\,(g)} \leftrightarrow CO_{2\,(aq)} \qquad (3.1)$$

The partial pressure of CO_2 (pCO_2) is that part of the total pressure exerted by a mixture of gases that is attributable to carbon dioxide (Ford & Williams, 1989).

Carbon dioxide and water combine to form carbonic acid (H_2CO_3):

$$CO_{2\,(aq)} + H_2O \leftrightarrow H_2CO_3 \qquad (3.2)$$

Some carbonic acid ionises to produce hydrogen carbonate, or bicarbonate, (HCO_3^-) and hydrogen (H^+) ions which lowers the pH of the solution:

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \qquad (3.3)$$

In turn, the hydrogen carbonate dissociates into carbonate (CO_3^{2-}) and hydrogen ions:

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \qquad (3.4)$$

This sequence describes the chemical reactions that would take place within a closed system. Only two phases, gas and liquid, interact and the solution is in the stationary, low energy state of equilibrium. This situation is rare in nature where most systems are open and the three phases of solid, liquid and gas, are able to react together (Ford & Williams, 1989). The weathering of limestone is an example of an open, three-phase system (Fig. 21, iii).

3.7 GROUNDWATER CHEMISTRY

3.7.1 Limestone weathering, solution and precipitation

The weathering of limestone rocks, at the surface and underground, can be summarised in the equation:

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \qquad (3.5)$$

The dissolution and precipitation of calcium carbonate ($CaCO_3$) is determined by the chemistry of the $CaCO_3 - H_2O - CO_2$ system which is explained in the following series of chemical processes:

In pure water, limestone in the form of $CaCO_3$ dissociates into calcium and carbonate ions:

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-} \qquad (3.6)$$

When precipitation in the form of rain or snow, enriched with atmospheric and soil-derived carbon dioxide enters the carbonate rocks, the carbonic acid produced reacts with the carbonate minerals and releases calcium and bicarbonate ions into solution:

$$CaCO_{3(s)} + H_2O + CO_2 \leftrightarrow Ca^{2+} + 2HCO_3^- \qquad (3.7)$$

When equation (3.6) is reversed and carbon dioxide is lost from the solution, calcium carbonate is precipitated:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_{3(s)} + CO_{2(g)} + H_2O \qquad (3.8)$$

In this way, the concentration of CO_2 in the water determines the extent of dissolution of calcium carbonate (Dreybodt, 1988).

3.7.2 Carbon Dioxide

Pure water has little effect on limestone and the solvent action which is necessary for dissolution is provided mainly by carbonic acid (H_2CO_3) (Ford & Williams, 1989). This weak acid is formed by the dissolution of gaseous carbon dioxide (Stumm & Morgan, 1996) although other sources of acidity such as humic acids exist which can aid the weathering process (Trudgill, 1985). Carbon dioxide is the most soluble of the standard atmospheric gases and its solubility is inversely proportional to temperature (Ford & Williams, 1989). pCO_2 is the CO_2 pressure in the gaseous phase in equilibrium with the water and the concentration of dissolved CO_2 increases with increasing pCO_2 that exists in the gas phase (White, 1988). The pCO_2 of ground waters is often many times greater than that of the atmosphere (Pearson *et al.*, 1978). CO_2 is present in the atmosphere at sea level, at approximately 0.0355% by volume in dry air and pCO_2 is expressed as 3.55×10^{-4} atm (log pCO^2) (Stumm & Morgan, 1996), although present day levels are reported as having risen to 0.0381% (Pearce, 2006).

The soil layer is an important producer and reservoir of biogenic CO_2 as well as being a store for CO_2 enriched rainwater. Organic carbon dioxide is produced in the soil by the respiration of plants and animals, and by the aerobic decay of organic matter. Concentrations of soil CO_2 can be from 10 to 30 times (0.3 – 1.0%) as high as atmospheric levels. This figure can rise to 2 – 10% CO_2 in some wet clay soils at depths of 1 – 2 metres from the surface (Trudgill, 1985). Atkinson & Smith (1976) and Atkinson (1977a) reported CO_2 concentrations ranging from 0.27 – 0.41% in the brown earth soils of the Mendip plateau. Atkinson (1977b) concluded that organic matter is also oxidised in the fissures and fractures of the vadose or unsaturated zone of the Mendip karst and suggested the term "ground air carbon dioxide" to distinguish it from CO_2 in the soil air. In joints totally or partially filled with mud, the average pCO_2 of 0.016 atm. was found to be 4.4 times greater than the cave air. The results of the study also suggested that organic matter was washed into fissures and joints by percolating water and that the decay of the material in a confined space would produce exceptionally high concentrations of CO_2. The flux of CO_2 into and out of a water body affects the saturation state of the solution with regard to the carbonate minerals within the water (Herman & Lorah, 1987).

3.8 THE HYDROGEOCHEMISTRY OF TUFA DEPOSITION

Two studies of calcite-precipitating springs in the Triassic limestones of West Germany revealed that calcite precipitation and a decrease in the concentration of soluble calcium were coincident with decreasing CO_2 concentrations in the springwater (Jacobson & Usdowski, 1975; Usdowski *et al.*, 1979). Supersaturation ratios (Ω) of almost 5 had to be reached, however, before calcite was precipitated. Tufa was deposited from the spring rising and throughout the length of the stream channel, but accumulation was greatest in turbulent, high-energy waterfall zones where CO_2 loss was greatest. These observations were similar to those of Dandurand *et al.* (1982) in a study of Jurassic and Cretaceous limestone springs in the French Pyrenees. Water samples were collected each month from July 1978 to June 1979. However, in their study, tufa was not precipitated at the spring risings. The spring water became supersaturated with respect to calcite downstream on the degassing of CO_2. Calcite was precipitated only at high calcite saturation ratio levels ($\Omega \approx 10$) when the nucleation barrier had been passed. Calcite (tufa) was found predominantly at the turbulent cascades and in the lower reaches of the streams within the flowing channel but migrated in all directions as the stream bed was built up with the deposits. This would suggest that the groundwater, on emergence, was at equilibrium or undersaturated with respect to calcite. Dandurand *et al*. (1982) concluded that calcite was initially precipitated but did not accumulate because nucleation was inhibited by an energy barrier which was passed only when the solution reached a high saturation state.

On a larger scale, Kempe & Emeis (1985), in an investigation of the chronology of the Plitvice Lakes system in Croatia, used hydrogeochemical methods to determine reasons for the deposition of travertine. Karst springs rise from Triassic and Jurassic dolomitic limestones and collect in lakes which have been ponded behind travertine dams. Water emerging at the springs was often initially supersaturated with respect to CO_2 and undersaturated with respect to calcite. The range of pH values of the spring water was from 7.3 to 8.3. Analysis of water from the spring risings was found to be at saturation or near-saturation with respect to calcite with SIc values from -0.03 to 0.74. The spring water became supersaturated as a result of CO_2 loss in the fast-flowing streams. Downstream, Ca^{2+} values ranged from 65.7 to 130.3 mg l^{-1}. pH, alkalinity (HCO_3^-) and $p$$CO_2$ all showed seasonal trends.

A study of a small tufa-depositing spring by Hoffer-French & Herman (1989) was one of a series of investigations into calcite precipitation carried out in the Cambrian and Ordovician karst limestones of Virginia, United States of America. Water sampling took place monthly from June 1985 to June 1986. A summary of the water analysis is shown in Table 5. The SIc began to rise to supersaturation levels downstream, coincident with an increase in pH and a drop in Ca^{2+} and HCO_3^- concentrations. Calcite precipitation did not occur instantaneously as supersaturation was reached and appeared to be kinetically inhibited. The critical supersaturation level for precipitation in the stream was SIc $\approx$ 0.5. The calcite saturation state was brought nearer to the critical level as a result of hydrological turbulence. There was only a slight seasonal variation in $p$$CO_2$ and calcite precipitation during the 12 month sampling period but Ca^{2+} and HCO_3^- concentrations decreased more noticeably during the summer months. Low-flow conditions and loss of CO_2 during the summer resulted in a high SIc $\approx$ 0.8-1.0, with calcite precipitation occurring in laminar sections of the stream. The spring waters were highly supersaturated with respect to CO_2 throughout the year and remained supersaturated along the full length of the 2.5 km flowpath of the stream.

A summary of the chemical results of the study by Hoffer-French & Herman (1989) and Dandurand *et al.* (1982) are shown in Table 5. Both sets of authors concluded that biological factors played only a minor role in the flux of CO_2 and that the deposition of tufa in the streams was driven by inorganic factors such as calcite supersaturation and turbulence at waterfalls and cascades where the physical degassing of CO_2 was enhanced.

Table 5. Summary of chemical analysis of tufa spring and stream water at 1. Roquefort-les-Cascades (from Dandurand *et al.* 1982) and 2. Falling Spring Run (from Hoffer-French & Herman, 1989). All solute concentrations are expressed as mg l^{-1}, n/d = no data presented.

Location	1.		2.	
Parameter	Spring	Stream	Spring	Stream
Temp. (°C)	10.7 – 11.1	8.0 – 13.5	14	9.5 – 19.0
pH	7.07 – 7.63	8.06 – 8.53	7.13	7.29 – 8.24
HCO_3	290.9 – 311.0	153 – 308	352	313 - 352
Ca	81.0 – 90.6	43 – 88.2	72.7	63.3 – 72.6
Mg	8.3 – 12.0	n/d	28.5	27.6 – 28.4
Na	1.1 – 1.6	n/d	0.6	0.6 – 1.5
K	0.1 – 0.2	n/d	1.1	1.0 – 1.6
Cl	2.4	n/d	1.2	1.2 – 3.1
SO_4	9.1 – 10.2	n/d	2.9	3.0 – 4.8
log pCO_2 (atm)	(-)1.68 – (-)2.24	(-)2.68 – (-)3.05	(-)1.37 – (-)1.75	(-)1.68 – (-)2.9
1. (Ω), 2. (SIc)	0.60 – 2.16	4.38 – 12.71	(-)0.36 – (-)0.02	(-)0.10 – (+)0.98

During an investigation by Baker & Simms (1998), actively-depositing tufa springs in the Mendip district of Somerset were only found in areas underlain by Jurassic and Triassic rocks. They found no tufa sites directly associated with the Carboniferous Limestone and attributed this to its high permeability and fissure flow and the rapid passage of water through the rock. The calcite supersaturation of water samples analysed in their study was explained by the long residence time of groundwater within the Jurassic Oolite formations which have low permeability and high porosity.

Tufa deposits and major springs in the Yorkshire Dales were investigated by Pentecost (1981, 1992). In contrast to the steeply dipping beds of the present East Mendip study area, the Carboniferous strata of the Yorkshire Dales are approximately horizontal and there are numerous allogenic and autogenic streams. Chemical analysis of several tufa-depositing streams revealed a narrow range of SIc values (0.94 – 1.12) at the springheads and a wide variation in other hydrochemical values. At Waterfall Beck, changes in the chemical composition of waters downstream revealed a fall in total CO_2, Ca^{2+} and HCO_3^- concentrations with a rise in pH and SIc. The results of the study revealed that supersaturation of the waters with calcite did not occur until 80 m downstream. In a comprehensive study of surface water chemistry in the Yorkshire Dales National Park, Pentecost (1992) reported a wide range of calcite saturation values throughout the various lithologies, with water from the pure Carboniferous Limestone (CKM) beds having a median SIc value of 1.74. Water from several tufa depositing springs in the region had high calcite saturation values (Ω 1.74 – 11.2) with a median of 5.2. However, many of the non tufa-depositing waters analysed also had values within the same range and water from adjacent catchments often displayed differing chemistries. The study revealed that allogenic waters rarely coincided with tufa deposition even though tufa is widespread in the Dales.

The Slade Brook in Gloucestershire rises from a number of Carboniferous Limestone springs and was the subject of a study by Pentecost *et al*. (2000). It has been recently notified (2003) as a SSSI because it contains nearly 700 metres of actively forming tufa dams (Wetherall, 2004). The brook was monitored over 14 months with water samples taken from two downstream sites. Tufa first occurred at about 50 m below the main spring source. Pentecost *et al*. (2000) reported that the rising groundwaters, which had a calcite saturation value of Ω 1.58, were close to equilibrium with the limestone source. Water temperature varied seasonally by only a few degrees Centigrade with no seasonal pattern in dissolved calcium levels. However, a significant negative correlation was found between the concentration of calcium and water discharge with the lowest levels of calcium occurring at the lowest discharge.

Many important sites of tufa deposition have recently been investigated in China, one of the world's largest areas of karst. Pentecost & Zhang (2001) provide a review of 88 active and inactive sites including several studies made at the Huanglong Ravine in the northwestern Sichuan Province. The Huanglong stream source is a group of several fault-bounded springs. The area is tectonically active. Tufa deposition begins approximately 250 m downstream from the spring risings which discharge with a pH of 6.5 and a temperature of 6ºC. In a study of the downstream hydrochemistry, Zaihua *et al.* (1995) reported that the slightly undersaturated rising spring water (SIc -0.08 to -0.20) had a calculated high partial pressure of CO_2 (log pCO_2 ~ 0.23 atm) and underwent changes in the Ca-CO_2 system. The changes, i.e. a fall in Ca with a rise in pH, and CO_2 loss from the water were consistent with a change in the SIc. These processes have also been observed by other workers in the field (e.g. Lu *et al.* 2000).

High altitude (> 2 000 m above sea level) travertine-depositing springs were investigated in the Yunnan Province of SW China by Liu *et al.* (2003). The study site was located within an area which had been subjected to intensive neotectonic movement and, as a consequence, the limestones were highly fractured with well-developed faults and fissures. Two of the three springs, which emerged at temperatures from 7.2 to 10.9ºC were found to have high concentrations of Ca^{2+} (191 and 193 mg l^{-1}) and HCO_3^- (699 and 708 mg l^{-1}) with a pH of 6.61 and 6.53, respectively. Conductivity readings were high (990 and 1009 µS cm^{-1}) and the SIc was -0.03 and -0.10. The correspondingly high pCO_2 of two of the springs (14 400 and 17 560 Pa) were considered to be too high to be the result of biological activity in the soil alone and that an endogenic supply of CO_2 was present in the water which was at considerably higher partial pressure than that of the atmosphere. The deposition of travertine took place at approximately 500 m downstream.

3.9 AIM

With regard to the previous studies, it is apparent that the carbonate chemistry of the spring water plays a major role in the deposition of tufa. It has been observed that Whitehole Farm Spring deposits tufa in its stream and that St. Dunstan's Well does not, therefore it was predicted that the carbonate chemistry of the water at Whitehole Farm Spring would be significantly different from the water at St. Dunstan's Well.

The aim of this section of the thesis was to investigate and compare the hydrogeochemical characteristics of two allogenic karst springs in adjacent and similar geological catchments; one spring is tufa-depositing (Whitehole Farm Spring) and the other is non tufa-depositing (St. Dunstan's Well). The aim was to be achieved by carrying out a quantitative chemical investigation of the two springs and their streams :

- Monthly water sampling at Whitehole Farm Spring and St. Dunstan's Well over an 18 month period.
- Chemical analysis of the water samples in the field and laboratory.
- Statistical and graphical analysis of the collected data.

The choice of chemical parameters for analysis was determined by the requirements of the Environment Agency for the Mells Valley S106. Both data sets were compared in order to determine key hydrogeochemical differences and trends which could influence the deposition or non-deposition of tufa. The data collected will provide a baseline for future chemical monitoring of springs in the Mells Valley.

3.10 MATERIALS AND METHODS

Water sampling was carried out at the beginning of each consecutive month from January 2002 to June 2003 at Whitehole Farm Spring (WHF) and St. Dunstan's Well (STDW). Two routine sampling points were established at each site, one located at the spring resurgence (point A), and the other located 100 metres downstream (point B).

3.10.1 Field methods

In order to minimise changes in basic water quality , temperature, pH, electrical conductivity, total dissolved solids (TDS), alkalinity (HCO_3) and dissolved oxygen (DO_2) were measured in the field using the following hand-held equipment:

• Temperature	Digital thermometer and probe
• pH	Jenway pH meter (model 3150)
• Conductivity and TDS	Jenway combination meter (model 4200)
• Alkalinity	Hach Digital Titrator (Model 16900-01)
• DO_2	Jenway meter (model 9200)

Prior to water sampling, the pH meter was calibrated using pH buffers 4.60 and 7.00. The combination conductivity/TDS meter was calibrated using a solution of 0.746 g of dried A.R. grade potassium chloride dissolved in 1 litre of deionised water to produce a conductivity of 1411 μS @ 25°C (Jenway, 4200 Operating Manual). Alkalinity was analysed by titration with 0.16M H_2SO_4 using bromocresol green/methyl red indicator (Hach, 1994). The DO_2

meter was calibrated with a zero oxygen solution prepared by mixing 2 g of sodium sulphite in 100 ml of deionised water (Jenway, 9200 Operating Manual).

3.10.2 Water sampling procedure

Water samples were first collected at each sampling point in a 750 ml polyethylene beaker which had previously been acid-washed with 0.1 M HCl and rinsed with deionised water. Care was taken not to disturb the stream bed when taking samples in order to minimise the sediment content. The samples were measured in the beaker for temperature, pH, electrical conductivity, total dissolved solids (TDS), alkalinity (HCO_3) and dissolved oxygen (DO_2) before pouring into 500 ml, acid-washed polyethylene bottles with screw-on caps. The bottles were rinsed three times in the stream water at each sampling point before adding the sample from the beaker. Bottles were completely filled to the brim in order to minimise head space and all air bubbles were eliminated. Field instruments were washed with deionised water between samplings. The filled bottles were stored on-site in an ice-packed cool-box and refrigerated overnight at 4°C before being transported, in the cool-box, to the laboratory the following day. Samples were not filtered, treated or diluted in any way and were analysed within 24 hours of sampling. The American Public Health Association (APHA, 1998) reported that only insignificant changes occur in the container within that time if the samples are correctly stored by the described procedure. On arrival at the laboratory, the samples for immediate analysis were brought to room temperature of approximately 21°C, and all other samples were stored in the refrigerator at 4°C.

3.10.3 Laboratory Methods

Chemical analyses were carried out in the laboratory at Bath Spa University. Using standard laboratory instruments and methods.

Calcium, magnesium, sodium, potassium, iron and manganese were determined by atomic absorption spectrophotometry (AAS) (APHA, 1998). Nitrate was measured with a specific ion meter using a nitrate ion selective electrode (ISE) combination sensor (APHA, 1998). Chloride was measured by titration with silver nitrate (APHA, 1998). Sulphate was determined turbidimetrically with barium chloride using a 1 cm cuvette in the spectrophotometer at 420 nm wavelength and orthophosphate was determined by the ascorbic acid method using a 5 cm cuvette at 880 nm wavelength (Radojević & Bashkin, 1999). Blank samples were prepared for all determinations. Details of techniques and equipment used are summarised in Table 6.

Table 6. – Summary of analytical procedures

Constituent	Method	Equipment (Model)
Calcium (Ca)	AAS	Varian SpectrAA 220FS
Magnesium (Mg)	AAS	Varian SpectrAA 220FS
Iron (Total Fe)	AAS	Varian SpectrAA 220FS
Manganese (Mn)	AAS	Varian SpectrAA 220FS
Sodium (Na)	AAS	Varian SpectrAA 220FS
Potassium (K)	AAS	Varian SpectrAA 220FS
Chloride (Cl)	Argentometric	Hach Digital Titrator 16900-01
Nitrate (NO_3)	ISE	Denver Model 225
Sulphate (SO_4)	Turbidimetric	LKB Ultraspec II
Phosphate (PO_4)	Colorometric	LKB Ultraspec II

3.10.4 Data analysis and statistics

Hydrogeochemical data, including the evaluation of theoretical partial pressures of carbon dioxide gas as pCO_2 ($10^{-3.5}$ atm) and the calcite saturation index (SIc), were analysed using WATEQ4F, a computer software program for calculating chemical equilibrium in natural waters (Ball *et al.*, 1987). SIc was calculated from pH, water temperature, calcium concentration, alkalinity and ion concentration Total hardness was calculated from the results of the separate determinations of calcium and magnesium by AAS, using the formula:

Hardness, mg l^{-1} $CaCO_3$ = 2.497 [Ca mgl^{-1}] + 4118 [Mg mgl^{-1}]

(APHA, 1998)

All data were statistically analysed using Minitab™ Release 13 for Windows® and Microsoft® Excel. The data were analysed for normality using the Anderson-Darling test (Sokal & Rohlf, 1995). All normally distributed data were analysed using the parametric tests, paired and 2-sample T-tests. pH was tested using the Kruskall-Wallis test of the medians and other non-parametric data were compared using the Wilcoxon Signed Rank test and the Mann-Whitney U-test (Pentecost, 1999b). Correlations between the data were examined using Pearson's correlation coefficients. All graphs were produced using Microsoft® Excel. Rainfall data for the East Mendip area and flow data for the springs was supplied by the Environment Agency and Hanson plc.

Sampling points were abbreviated in the following way:

- WHF A – Whitehole Farm Spring resurgence
- WHF B – Whitehole Farm Spring 100 m downstream
- STDW A – St. Dunstan's Well resurgence
- STDW B – St. Dunstan's Well 100 m downstream

3.11 RESULTS

3.11.1 Precipitation and flow rates

Total monthly precipitation and mean daily flow rates are illustrated in Figs 22 and 23. There was a marked difference between the amount of flow at Whitehole Farm Spring and St. Dunstan's Well (Fig. 23). The flow at St. Dunstan's Well had a daily range of 3.5 – 26.7 ML d^{-1} and the flow range at Whitehole Farm Spring was 0.18 – 2.3 ML d^{-1}. The Mann-Whitney U-test revealed a significant difference between the flow rates of the two springs ($p < 0.001$). The mean daily flow at St. Dunstan's Well (11.58 ML d^{-1}) was over twelve times higher than that of Whitehole Farm Spring (0.95 ML d^{-1}) with a wider and higher range. There are rainfall and flow peaks in February 2002, May 2002, October 2002 and January 2003 .

The October peak in rainfall (Fig. 22), unlike February 2002, did not result in an immediately elevated flow rate at either spring and displays a time lag of approximately one month. However, by November (Fig. 23) the flow rates had begun to rise at both springs until January (Fig. 23). The flow at St. Dunstan's Well took longer to subside than the flow at Whitehole Farm Spring.

The temporal relationship between rainfall and flow rates at the two springs over the study period is displayed in Fig. 24. The flow rates at both springs show the same changes in trend and correlate with the rainfall data.

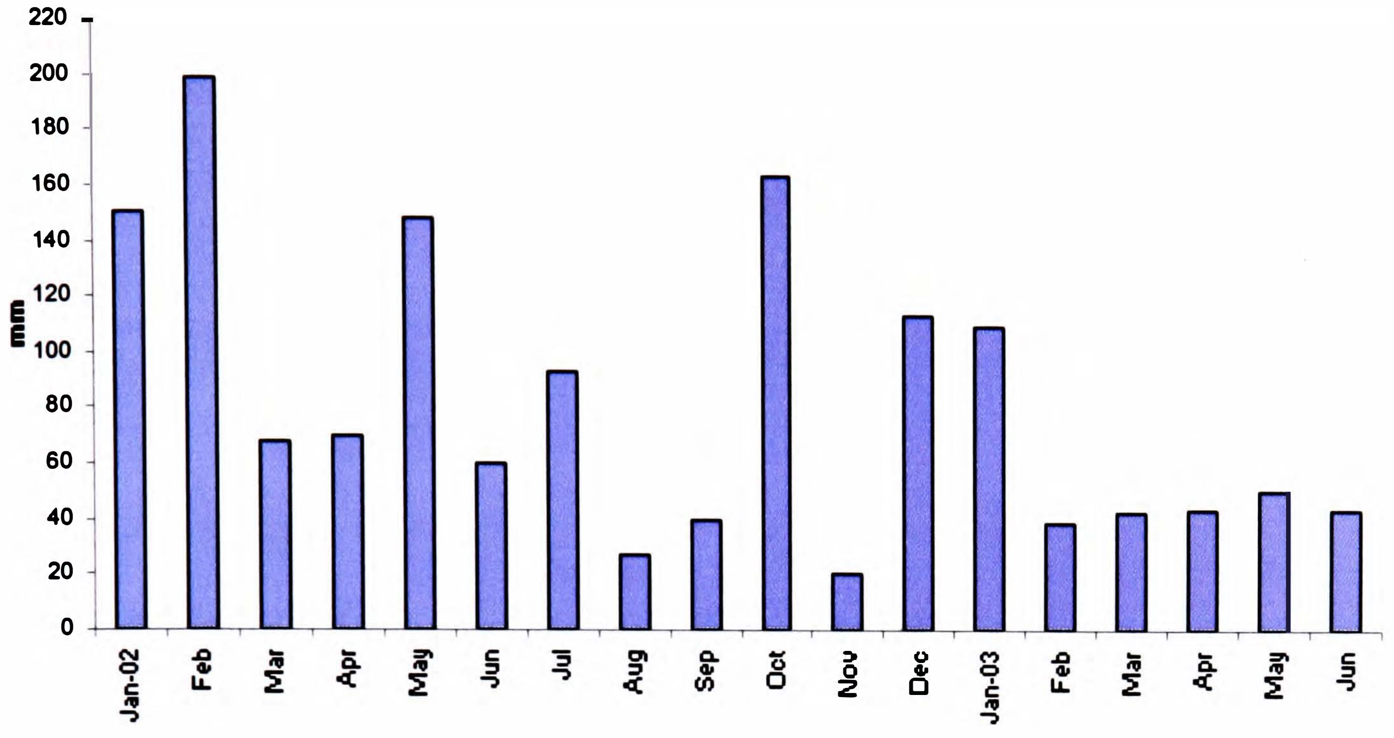


Fig. 22. Total monthly precipitation in millimetres for the East Mendip area during the study period January 2002 - June 2003.

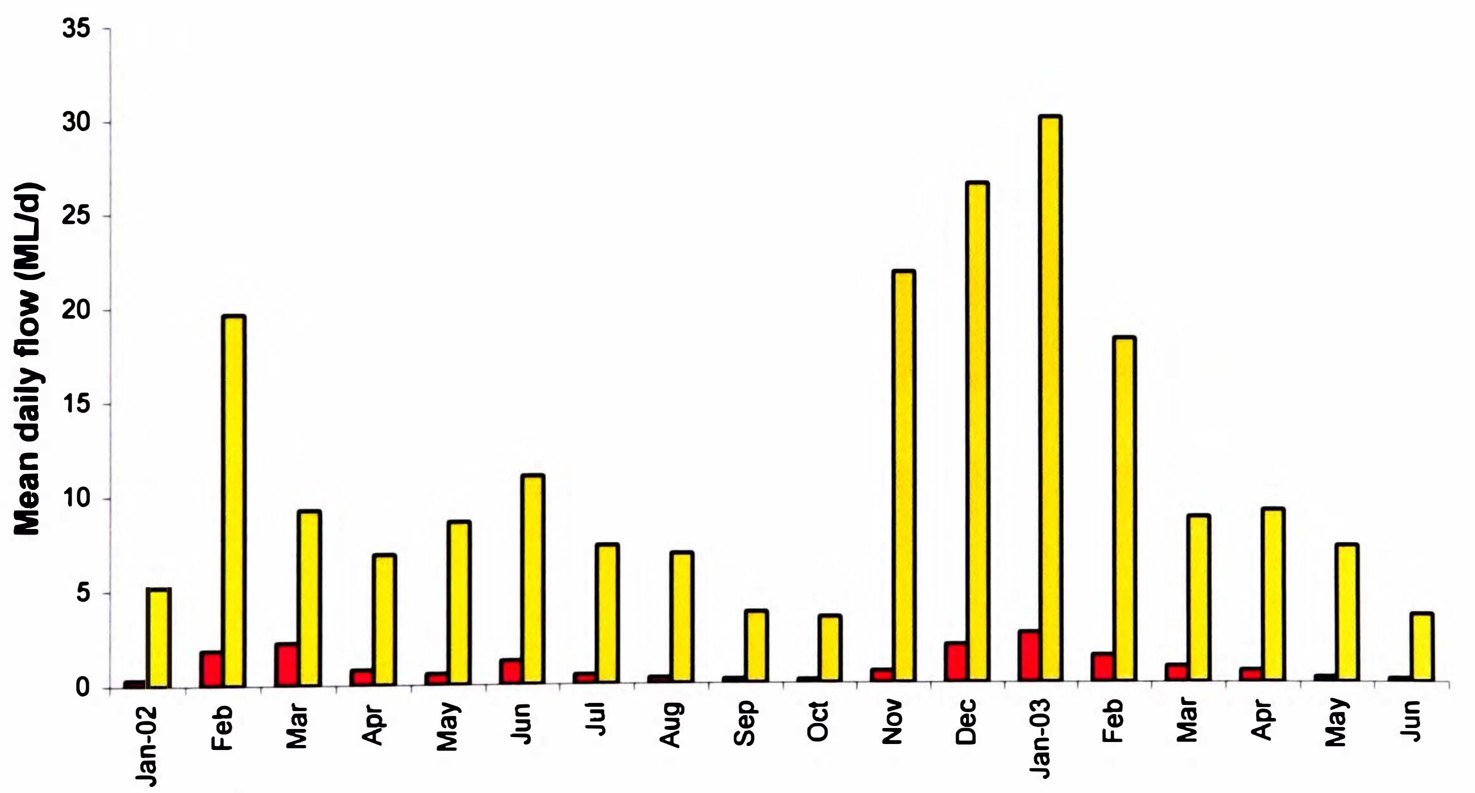


Fig. 23. Calculated mean daily flow (ML d^{-1}) on sampling dates at Whitehole Farm Spring (pink columns) and St. Dunstan's Well (yellow columns)

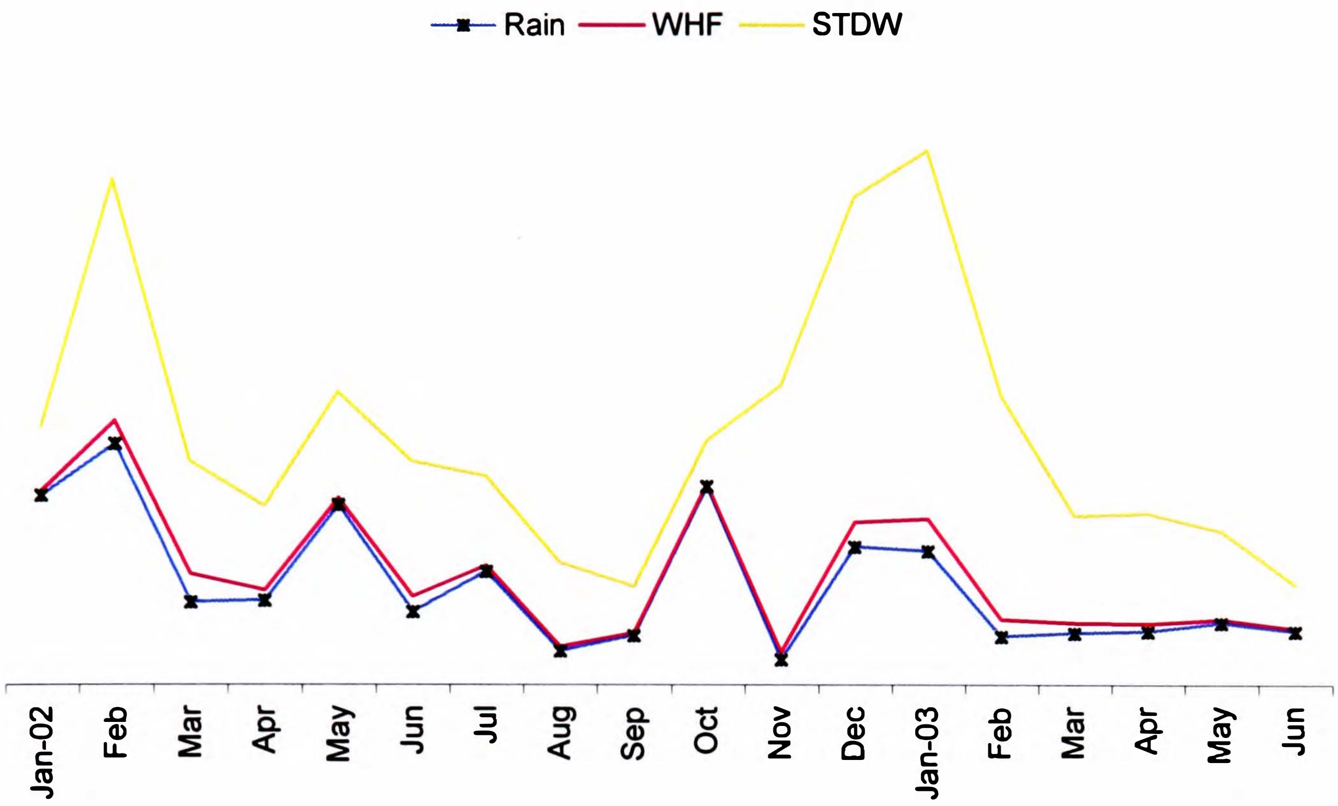


Fig. 24. Line graph to demonstrate the temporal relationship between rainfall (blue) and flow rates at Whitehole Farm Spring (pink) and St. Dunstan's Well (yellow) using modified data (y-axis represents quantity).

3.11.2 Hydrogeochemical data

Tables 7 – 10 show the summarised results of the hydrogeochemical and statistical analysis of the measured parameters. Both spring waters were characterised as being of the calcium – bicarbonate type (Ca – HCO_3) as calcium was the major cation and bicarbonate was the major anion. The levels of all parameters changed continually throughout the study period.

Table 7. Summarised results (mean, standard error (SE) and range) of chemical and physical analysis of the two spring resurgences. KW = Kruskall Wallis test, MW = Mann Whitney, T = 2 sample t-Test, PT = Paired t-test, W = Wilcoxon Signed Rank test. Statistically significant differences between samples (Sig) are shown as *** p = 0.001, ** p = 0.01, * p = 0.05, ns = not significantly different. n = no. of samples.

	Whitehole Farm Spring A	n = 18	**St. Dunstan's Well A**	n= 18	**Statistics**	
Parameter	Mean ± SE	Range	Mean ± SE	Range	Test	Sig
pH	7.0 ± 0.08	6.6 – 7.7	7.0 ± 0.08	6.8 – 7.9	KW	ns
Cond (μs cm^{-1})	574 ± 8.9	515 – 638	437 ± 17.4	253 – 519	MW	***
TDS (mg l^{-1})	344 ± 5.3	312 – 382	262 ± 10.48	151 – 316	T	***
DO_2 (mg l^{-1})	7.53 ± 0.28	4.7 – 10.0	9.9 ± 0.18	8.1 – 10.8	T	***
Water temp (°C)	9.9 ± 0.04	9.6 – 10.1	9.7 ± 0.14	8.4 – 10.7	T	ns
Alkalinity (mg l^{-1})	263 ± 4.09	230 – 300	206 ± 10.41	90 – 262	T	***
T. hardness (mg l^{-1})	317 ± 8.44	243 – 369	236 ± 7.49	196 – 324	T	***
Calcium (mg l^{-1})	112 ± 3.35	81 – 134	80 ± 2.7	66 – 108	T	***
Magnesium (mg l^{-1})	8.2 ± 0.55	3.4 – 14.5	7.9 ± 0.56	3.7 – 13.2	T	ns
Sodium (mg l^{-1})	7.0 ± 0.12	5.7 – 7.5	8.9 ± 0.32	6.5 – 12.4	MW	***
Potassium (mg l^{-1})	2.79 ± 0.09	2.2 – 3.3	3.4 ± 0.14	2.4 – 4.7	T	**
Iron (mg l^{-1})	0.021 ± 0.004	0 – 0.072	0.038 ± 0.004	0.017 – 0.074	MW	***
Nitrate (mg l^{-1})	7.5 ± 0.22	5.9 – 9.7	4.0 ± 0.15	2.9 – 5.0	T	***
Sulphate (mg l^{-1})	12.2 ± 0.47	9.4 – 16.7	15.0 ± 1.07	7.4 – 25.6	T	*
Phosphate (mg l^{-1})	0.015 ± 0.002	0 – 0.028	0.026 ± 0.004	0.004 – 0.078	T	*
Chloride (mg l^{-1})	15.2 ± 0.22	13.4 – 17.1	13.4 ± 0.59	6.0 – 16.9	T	**
SIc	-0.17 ± 0.08	-0.68 – 0.47	-0.33 ± 0.08	-0.73 – 0.61	MW	ns
log pCO_2 (atm)	-1.36 ± 0.10	-0.75 – (-)2.68	-1.43 ± 0.30	-0.57 –(-) 5.72	MW	ns
Flow (ML d^{-1})	0.95 ± 0.19	0.18 – 2.65	11.58 ± 1.93	3.54 – 30.24	MW	***

Table 8. Summarised results (mean, standard error (SE) and range) of chemical and physical analysis of the two sampling points at Whitehole Farm Spring. KW = Kruskall Wallis test, MW = Mann Whitney, T = 2 sample t-Test, PT = Paired t-test, W = Wilcoxon Signed Rank test. Statistically significant differences between samples (Sig) are shown as *** p = 0.001, ** p = 0.01, * p = 0.05, ns = not significantly different.

	Whitehole Farm Spring A		**Whitehole Farm Spring B**		**Statistics**	
Parameter	Mean ± SE	Range	Mean ± SE	Range	Test	Sig
pH	7.0 ± 0.08	6.6 – 7.7	7.7 ± 0.10	7.0 – 8.5	KW	***
Cond (µs cm^{-1})	574 ± 8.9	515 – 638	536 ± 11.1	458 – 635	PT	**
TDS (mg l^{-1})	344 ± 5.3	312 – 382	323 ± 7.7	273 – 381	PT	*
DO_2 (mg l^{-1})	7.53 ± 0.28	4.7 – 10.0	10.3 ± 0.21	8.3 – 11.8	PT	***
Water temp (°C)	9.9 ± 0.04	9.6 – 10.1	10.4 ± 0.26	8.4 – 12.6	PT	*
Alkalinity (mg l^{-1})	263 ± 4.09	230 – 300	243 ± 4.92	211 – 300	PT	**
T. hardness (mg l^{-1})	317 ± 8.44	243 – 369	288 ± 7.76	229 – 348	PT	***
Calcium (mg l^{-1})	112 ± 3.35	81 – 134	104 ± 3.08	80 – 125	PT	***
Magnesium (mg l^{-1})	8.2 ± 0.55	3.4 – 14.5	7.23 ± 0.28	5.0 – 9.3	PT	ns
Sodium (mg l^{-1})	7.0 ± 0.12	5.7 – 7.5	6.8 ± 0.15	5.2 – 7.5	W	***
Potassium (mg l^{-1})	2.79 ± 0.09	2.2 – 3.3	2.8 ± 0.09	1.9 – 3.5	W	***
Iron (mg l^{-1})	0.021 ± 0.004	0 – 0.072	0.033 ± 0.01	0 – 0.198	W	***
Nitrate (mg l^{-1})	7.5 ± 0.22	5.9 – 9.7	7.16 ± 0.24	5.7 – 9.9	PT	*
Sulphate (mg l^{-1})	12.2 ± 0.47	9.4 – 16.7	11.7 ± 0.54	8.9 – 16.9	W	***
Phosphate (mg l^{-1})	0.015 ± 0.002	0 – 0.028	0.011 ± 0.002	0 – 0.029	PT	ns
Chloride (mg l^{-1})	15.2 ± 0.22	13.4 – 17.1	15.0 ± 0.28	12.5 – 16.8	PT	ns
SIc	-0.17 ± 0.08	-0.68 – 0.47	0.43 ± 0.10	-0.27 – 1.26	PT	***
log pCO_2 (atm)	-1.36 ± 0.10	-0.75 –(-)2.68	-1.25 ± 0.12	-0.43 –(-)2.46	PT	ns

Table 9. Summarised results (mean, standard error (SE) and range) of chemical and physical analysis of samples 100 m downstream. KW = Kruskall Wallis test, MW = Mann Whitney, T = 2 sample t-Test, PT = Paired t-test, W = Wilcoxon Signed Rank test. Statistically significant differences between samples (Sig) are shown as *** p = 0.001, ** p = 0.01, * p = 0.05, ns = not significantly different.

	Whitehole Farm Spring B		**St. Dunstan's Well B**		**Statistics**	
Parameter	Mean ± SE	Range	Mean ± SE	Range	Test	Sig
pH	7.7 ± 0.10	7.0 – 8.5	7.5 ± 0.08	7.1 – 8.2	KW	ns
Cond ($\mu s\ cm^{-1}$)	536 ± 11.1	458 – 635	409 ± 10.6	343 – 519	T	***
TDS ($mg\ l^{-1}$)	323 ± 7.7	273 – 381	247 ± 6.07	206 – 311	MW	***
DO_2 ($mg\ l^{-1}$)	10.3 ± 0.21	8.3 – 11.8	10.5 ± 0.16	9.6 – 11.8	T	ns
Water temp (°C)	10.4 ± 0.26	8.4 – 12.6	10.2 ± 0.29	8.5 – 12.4	T	ns
Alkalinity ($mg\ l^{-1}$)	243 ± 4.92	211 – 300	188 ± 4.13	150 – 220	T	***
T. hardness ($mg\ l^{-1}$)	288 ± 7.76	229 – 348	212 ± 7.0	147 – 257	T	***
Calcium ($mg\ l^{-1}$)	104 ± 3.08	80 – 125	72 ± 2.59	52 – 89	T	***
Magnesium ($mg\ l^{-1}$)	7.23 ± 0.28	5.0 – 9.3	8.12 ± 0.61	3.4 – 14.7	T	ns
Sodium ($mg\ l^{-1}$)	6.8 ± 0.15	5.2 – 7.5	7.8 ± 0.16	6.4 – 9.1	T	***
Potassium ($mg\ l^{-1}$)	2.8 ± 0.09	1.9 – 3.5	3.14 ± 0.11	2.3 – 4.2	MW	*
Iron ($mg\ l^{-1}$)	0.033 ± 0.01	0 – 0.198	0.054 ± 0.009	0.016 – 0.137	MW	**
Nitrate ($mg\ l^{-1}$)	7.16 ± 0.24	5.7 – 9.9	4.08 ± 0.13	3.2 – 4.8	T	***
Sulphate ($mg\ l^{-1}$)	11.7 ± 0.54	8.9 – 16.9	14.8 ± 0.85	9.1 – 23.7	MW	*
Phosphate ($mg\ l^{-1}$)	0.011 ± 0.002	0 – 0.029	0.032 ± 0.003	0.006 – 0.054	MW	***
Chloride ($mg\ l^{-1}$)	15.0 ± 0.28	12.5 – 16.8	14.4 ± 0.41	9.9 – 17.0	T	ns
SIc	0.43 ± 0.10	-0.27 – 1.26	-0.011 ± 0.079	-0.57 – 0.81	T	**
log pCO_2 (atm)	-1.25 ± 0.12	-0.43 –(-)2.46	-1.071 ± 0.093	-0.56 –(-)2.07	MW	ns

Table 10. Summarised results (mean, standard error (SE) and range) of chemical and physical analysis of the two sampling points at St. Dunstan's Well. KW = Kruskall Wallis test, MW = Mann Whitney, T = 2 sample t-Test, PT = Paired t-test, W = Wilcoxon Signed Rank test. Statistically significant differences between samples (Sig) are shown as *** p = 0.001, ** p = 0.01, * p = 0.05, ns = not significantly different.

	St. Dunstan's Well A		St. Dunstan's Well B		Statistics	
Parameter	Mean ± SE	Range	Mean ± SE	Range	Test	Sig
pH	7.0 ± 0.08	6.8 – 7.9	7.5 ± 0.08	7.1 – 8.2	KW	***
Cond (μs cm^{-1})	437 ± 17.4	253 – 519	409 ± 10.6	343 – 519	PT	***
TDS (mg l^{-1})	262 ± 10.48	151 – 316	247 ± 6.07	206 – 311	PT	***
DO_2 (mg l^{-1})	9.9 ± 0.18	8.1 – 10.8	10.5 ± 0.16	9.6 – 11.8	PT	***
Water temp (°C)	9.7 ± 0.14	8.4 – 10.7	10.2 ± 0.29	8.5 – 12.4	PT	**
Alkalinity (mg l^{-1})	206 ± 10.41	90 – 262	188 ± 4.13	150 – 220	PT	ns
T. hardness (mg l^{-1})	236 ± 7.49	196 – 324	212 ± 7.0	147 – 257	PT	**
Calcium (mg l^{-1})	80 ± 2.7	66 – 108	72 ± 2.59	52 – 89	PT	**
Magnesium (mg l^{-1})	7.9 ± 0.56	3.7 – 13.2	8.12 ± 0.61	3.4 – 14.7	PT	ns
Sodium (mg l^{-1})	8.9 ± 0.32	6.5 – 12.4	7.8 ± 0.16	6.4 – 9.1	W	**
Potassium (mg l^{-1})	3.4 ± 0.14	2.4 – 4.7	3.14 ± 0.11	2.3 – 4.2	W	ns
Iron (mg l^{-1})	0.038 ± 0.004	0.017 – 0.074	0.054 ± 0.009	0.016 – 0.137	W	***
Nitrate (mg l^{-1})	4.0 ± 0.15	2.9 – 5.0	4.08 ± 0.13	3.2 – 4.8	PT	ns
Sulphate (mg l^{-1})	15.0 ± 1.07	7.4 – 25.6	14.8 ± 0.85	9.1 – 23.7	W	ns
Phosphate (mg l^{-1})	0.026 ± 0.004	0.004 – 0.078	0.032 ± 0.003	0.006 – 0.054	PT	ns
Chloride (mg l^{-1})	13.4 ± 0.59	6.0 – 16.9	14.4 ± 0.41	9.9 – 17.0	PT	ns
SIc	-0.33 ± 0.08	-0.73 – 0.61	-0.011 ± 0.079	-0.57 – 0.81	PT	***
log pCO_2 (atm)	-1.43 ± 0.30	-0.57 – (-)5.72	-1.071 ± 0.093	-0.56 – (-)2.07	PT	***

3.11.3 Physical parameters

3.11.3.1 pH

There were no significant differences in pH values between the two spring resurgences or at 100 metres downstream. However, there was an increase in mean pH values between the upper and lower sampling points of both springs and there was a significant difference between the upper and lower sampling points at each spring ($p < 0.001$).

3.11.3.2 Conductivity and total dissolved solids (TDS)

Conductivity and TDS were significantly different ($p < 0.001$) at both springs and the downstream sampling points. The conductivity range at WHF A was higher but narrower than that of STDW A with the mean at WHF A being 137 $\mu S\ cm^{-1}$ higher than that of STDW A. There was an approximate 6% reduction in conductivity and TDS at the downstream sampling points. Both mean conductivity and TDS values decreased between the upper and lower sampling points of both springs.

3.11.3.3 Dissolved oxygen

Dissolved oxygen values at WHF A were consistently lower than at the downstream sampling point. This result was similar at St. Dunstan's Well where oxygen levels were low at the resurgence but had risen at the downstream sampling point. There was a significant difference ($p < 0.001$) between the oxygen levels at the resurgences of both springs but not at the downstream sampling points. STDW A had a higher mean and range than WHF A.

3.11.3.4 Water temperature

There were no significant differences between the water temperatures of the springs at sampling point A where the mean water temperature was similar (STDW A, 9.7 °C; WHF A, 9.9 °C). Over the eighteen month sampling period, the temperature at Whitehole Farm Spring remained stable whereas the temperature at St. Dunstan's Well was more variable with a marked seasonal trend, i.e. a rise from April to June and a fall from October to January. This trend occurred at both sampling points. However, STDW A had the widest temperature range (8.4 to 10.7°C). Mean water temperature increased by 0.5° C downstream at both springs.

3.11.4 Carbonate ions

3.11.4.1..Alkalinity (HCO_3)

Within the pH range of the springs, alkalinity has been measured as HCO_3^- There were significant differences in alkalinity ($p < 0.001$) between the spring resurgences and the downstream sampling points. St. Dunstan's Well had a lower overall mean alkalinity than Whitehole Farm Spring and a wider range of values. In both streams, alkalinity fell 8 – 9% beween the resurgence and downstream sampling points.

3.11.4.2 Calcium

Mean calcium values were consistently higher at WHF A (112 mg l^{-1}) than at STDW A (80 mg l^{-1}). Similarly, mean calcium values were higher at WHF B (104 mg l^{-1}) than at STDW B (72 mg l^{-1}). In both streams, alkalinity had fallen by 8 mg l^{-1} at the downstream sampling points. There were significant differences ($p < 0.001$) between values at both sampling points.

3.11.4.3 Magnesium

Throughout the study period, overall magnesium concentrations were low at both springs (max 14.7 mg l^{-1}). There were no significant differences between values at any of the sampling points.

3.11.5 Non-carbonate ions

The measured non-carbonate ions present in the water at the two springs were, in order of abundance, chloride, sulphate, sodium, nitrate and potassium.

Mean values for chloride were significantly different ($p < 0.01$) only between the two spring resurgences where levels were higher at Whitehole farm Spring. Chloride levels were particularly variable at St. Dunstan's Well which had a wider range of values at both sampling points. Downstream values were similar at WHF B and STDW B but not significantly different. Mean sodium values at both springs were low. However, there was a significant difference between sodium levels at all sampling points with those of St. Dunstan's Well being higher.

Sulphate values were similar at both springs with only a slight difference between them ($p < 0.05$) but were significantly different ($p < 0.001$) between the resurgence and lower sampling point at Whitehole Farm Spring.

Comparison of nitrate shows that mean values were consistently lower at both STDW A and STDW B than at WHF A and WHF B and the difference between the nitrate values at both sampling points was significant ($p < 0.001$).

Potassium levels were low at both springs with a maximum value of 4.2 mg l^{-1} at STDW B.

3.11.6 Manganese, iron and phosphate

Manganese, iron and orthophosphate were all present in the water samples in trace amounts but manganese was below the detection limit (0.02 mg l^{-1}) at each analysis for Whitehole Farm Spring and only in a detectable amount (0.03 mg l^{-1}) in one sample at St. Dunstan's Well. Iron levels at both sampling points at St. Dunstan's Well were higher and significantly different ($p < 0.001$) from those at Whitehole Farm Spring. Iron levels also rose at the downstream sampling points of both springs. Mean phosphate values were higher at St. Dunstan's Well than Whitehole Farm Spring with significant differences between the downstream sampling points.

3.11.7 Calculated parameters

3.11.7.1 Total hardness (as $CaCO_3$)

The mean total hardness at STDW A was 81 mg l^{-1} lower than at WHF A and St. Dunstan's Well displayed a wider but lower range of values than Whitehole Farm Spring. The difference between them was significant ($p < 0.001$). Mean levels were lower for both springs at the downstream sampling points and again there was a significant difference between them ($p < 0.001$).

3.11.7.2 Carbon dioxide

Apart from one anomalous high level in February 2002 (STDW A, -5.72 atm), both springs were saturated with respect to atmospheric CO_2 at each sampling point. At St. Dunstan's Well there was a significant difference ($p < 0.001$) between the upstream and downstream samples. The mean pCO_2 was higher and and the range of values at St. Dunstan's Well was wider than Whitehole Farm Spring.

3.11.7.3 Saturation index for calcite (SIc)

The calculated SIc for the two springs shows that the spring resurgence at WHF A was undersaturated with respect to calcite on 12 of the 18 monthly samplings. It was saturated or supersaturated on six samplings, most noticeably during the months of October (SIc = 0.04), November (SIc = 0.47), December (SIc = 0.4) and January (SIc = 0.2). WHF A was also supersaturated in June 2003 (SIc = 0.34). The mean SIc for WHF A was –0.17. STDW A was supersaturated in October (SIc =0.29) and November (SIc = 0.16) but undersaturated in all other samples except June 2003 (SIc = 0.61) and had a mean SIc value of –0.33. There was no significant difference in SIc at the resurgences. For the downstream samples, WHF B was only undersaturated on three samplings – May (SIc = -0.16), June (SIc = -0.18) and July 2002 (SIc =-0.27) with a mean value of 0.43. STDW B, however, was undersaturated on twelve samplings – January to July 2002 and January to May 2003. The mean SIc was –0.011. There was a significant difference ($p < 0.001$) between the resurgence and downstream samples at both springs.

3.11.8 Correlations

Tables 11a – 11f show the most significant correlations ($p < 0.001$ and $p < 0.01$) between measured and calculated parameters at both sampling points of the springs. If the correlations which have arisen as a result of being components of equation calculation such as SIc/pH, conductivity/TDS, Ca/TH ($CaCO_3$) and pCO_2/HCO_3 are disregarded, the only result common to both springs and at all sampling points is the negatively correlated temperature and dissolved oxygen. At the individual sampling points, only St. Dunstan's Well B shows correlations which are not related to the carbonate system (Table 11d) where iron is negatively correlated with TDS and positively with calcium. Chloride and phosphate are also positively correlated at the lower sampling point.

Tables 11a – 11f. Significant correlations between parameters at the individual sampling points using Pearson's correlation coefficient (r-values) and degrees of significance. *** = $p < 0.001$, ** = $p < 0.01$. (- indicates a negative correlation). Cond = conductivity, DO_2 = dissolved oxygen, Alk = alkalinity, Temp = water temperature, TDS = total dissolved solids, TH = total hardness, Ca = calcium, SIc = saturation index (calcite), pCO_2 = partial pressure CO_2, Fe = iron, Cl = chloride, PO_4 = phosphate, NO_3 = nitrate, SO_4 = sulphate.

Table 11a. WHF A

WHF A	pH	Cond	DO_2	Alk	TH	Ca
TDS		0.998 ***				
Temp			-0.633 **			
Ca					0.885 ***	
SIc	0.987 ***					
pCO_2				0.689 **	-0.777 ***	-0.744 ***

Table 11b. WHF B

WHF B	pH	cond	DO_2	Alk	TH
TDS		0.999 ***			
Temp			-0.734 ***		
Ca					0.897 ***
Slc	0.933 ***				
pCO_2				0.659 **	

Table 11c. STDW A

STDW A	pH	cond	TDS	DO_2	TH
Cond			1.000 ***		
Temp		0.704 **	0.704 **	-0.734 **	
Ca					0.898 ***
Slc	0.933 ***				

Table 11d. STDW B

STDW B	pH	cond	TDS	DO_2	TH	Ca	PO_4
TDS		0.979 ***					
Temp				-0.840 ***			
Ca					0.900 ***		
Fe			-0.637 ***			0.643 **	
Cl							0.621 **
Slc	0.965 ***						

Correlations between the upper and lower sampling points at St. Dunstan's Well (Table 11e) and Whitehole Farm Spring (Table 11f) revealed a number of results unrelated to the carbonate system. Both sulphate and chloride values at Whitehole Farm resurgence were correlated with nitrate values downstream. At St. Dunstan's Well, sulphate values at the resurgence were correlated with potassium and phosphate values downstream.

Table 11e. St. Dunstan's Well – sampling points A v B

A B	pH	cond	DO_2	SO_4	PO_4	Slc
pH	0.818 ***					0.790 ***
DO_2		-0.665 **				
temp		0.618 **	-0.833 ***			
K				0.623 **		
SO_4					0.623 **	
Slc	0.796 ***					
$p$$CO_2$						0.771 ***

Table 11f. Whitehole Farm Spring – sampling points A v B

A B	pH	temp	DO_2	Alk	Ca	Fe	NO_3	SO_4	Cl	Slc
pH	0.805 ***									
Temp		0.873 ***	-0.624 **							
TDS				-0.656 **						
TH					0.853 ***					
Ca					0.851 ***					
Fe						0.854 ***				
NO_3							0.750 ***	0.770 ***	0.620 ***	
Cl									0.794 ***	
Ic	0.805 ***									0.786 ***

3.12 DISCUSSION

The results of the hydrogeochemical investigation have shown that although the two springs are closely located within the same outcrop of Carboniferous Limestone, there are considerable differences between not only the carbonate chemistry, but the overall water chemistries of the two karst springs. The main chemical differences between the water at the two resurgences were that Whitehole Farm Spring had higher levels of HCO_3, CO_3, Ca, total hardness, NO_3 and conductivity/TDS with St. Dunstan's Well being higher in DO_2, Mg, Na, K, Fe, SO_4, PO_4. The were also more differences between the upper and lower sampling points at St. Dunstan's Well than at Whitehole Farm Spring. Both springwaters are of simliar Ca – HCO_3 type which signifies dissolution of the calcite-rich Carboniferous Limestone bedrock and the influence of the limestone aquifer. The lower conductivity readings at St. Dunstan's Well are indicative of the lower levels of the two major ions, Ca^{2+} and HCO_3^- in the water. The two springs are both allogenic with similar hydrogeological processes and fed, in the most part, by sinking streams flowing overland from their upper Old Red Sandstone catchments. However, flow rates at St. Dunstan's Well were at least ten times higher than at Whitehole Farm Spring over the study period, which indicates that St. Dunstan's Well has a much larger catchment area and that percolation water and other sinking streams have a greater contribution to recharge than at Whitehole Farm Spring. Rainfall and flow rates have a direct influence on the carbonate system parameters at both springs although the effect is dampened to some extent at Whitehole Farm Spring by the existence of the settling tank at the resurgence.

It would be expected, due to their close proximity, that calcium levels in solution would be similar at the two resurgences. It has been reported in Chapters 1 & 2 that St. Dunstan's Well is an example of a more mature karst system with a well-developed network of caves and conduits behind the rising, therefore, during its travel underground through the Fairy Cave system, the flow of recharge water to St. Dunstan's Well is more likely to be turbulent causing degassing of CO_2 and deposition of $CaCO_3$ as spelaeothem flowstone in the open cave system (Pentecost, 1992). As stated in section 3.5, the nucleation and growth of calcite crystals at low saturation levels can only take place heterogenously in contact with a compatible solid, for example, flowstone covering the floor and walls of the caves (pers. obs.). As a result, the resurging water would be lower in calcium than that of Whitehole Farm Spring where the system is closed until the water first degasses CO_2 as it emerges from at the settling tank (Fig. 10). Calcium levels decrease at Whitehole Farm Spring following degassing of CO_2 at the tufa terraces and cascades (Fig. 11). However, although dissolved calcium levels are lower at St. Dunstan's Well than at Whitehole Farm Spring, they are still within the range for potential calcite precipitation as reported by some workers (e.g. Pentecost, 1981; Hoffer-French & Herman, 1989; Taylor *et al.* 2004).

With regard to NO_3^- levels at Whitehole Farm Spring, agricultural changes in the catchment from permanent pasture to annual arable cultivation could have resulted in the rapid passage of nitrogen fertilisers into the karst aquifer. Periodic high levels of NO_3 (> 50 mg l^{-1}) coinciding with heavy rainfall and ploughing have been noted in previous fieldwork (pers. obs.). The soluble NO_3^- would be available to plants within the stream and encourage the growth of algae, bryophytes and terrestrial plants which grow within the stream channel. The lower flow rates and discharge volume at Whitehole Farm Spring would enhance this effect. Agricultural chemicals or pollution could be the source of PO_4^{2-}, K^+, SO_4^{2-} and Cl^- in the samples from St. Dunstan's Well. Some of the constituents, such as Na^+, K^+, Fe^2+ and SO_4^{2-} could have resulted from the weathering of the volcanic rocks which form the core of the Beacon Hill and are currently being extracted at Moon's Hill Quarry (Figs. 3 & 12) in the upper catchment of St. Dunstan's Well (Chapter 2).

The resurgence at St. Dunstan's Well is natural and unmodified (Figs 7 & 8) unlike Whitehole Farm Spring which enters a sediment settling tank (Fig. 10). The desired action of the settling tank at Whitehole Farm Spring is to remove sediment particles such as silt and clay and therefore the water emerges with extremely low (barely measurable) suspended solids. The tank also acts as a buffer against erosive storm flow down the course of the stream. The natural rising at St. Dunstan's Well, however, is subject to episodes of storm flow and high suspended solids throughout the year (pers. obs). On these occasions the water has been travelling too rapidly to undergo natural filtration underground and emerges highly coloured often containing fine silt and clay sediment from the upper catchment. (pers obs) This is deposited on the stream bed and forms an unstable surface which is unsuitable for tufa deposition. Coatings of clay-like materials can retard the deposition of $CaCO_3$ (Picknett *et al.* 1976). Also, during these events, run-off from the adjacent agricultural fields can enter the stream below the waterfall to contribute to the suspended sediment and dissolved solids load. There are higher levels of all measured non-carbonate ions, except NO_3, at St. Dunstan's Well and it has previously been reported in laboratory studies that foreign particles in solution, such as Mg^{2+} and PO_4^{3-} can inhibit calcite crystal formation (Picknett, 1964; Reddy, 1983; Zhang & Dawe, 2000), although it is not known at what concentration this occurs in a field context. There are moderate amounts of non-carbonate ions and trace elements present in the water at Whitehole Farm Spring but none appear to have an inhibitory effect on tufa deposition.

The hydrogeochemical processes at Whitehole Farm Spring revealed in this study are comparable with those of other workers including Pentecost (1981), Dandurand *et al.* (1982), Zaihua *et al.* (1995), Lorah & Herman (1988), Hoffer-French & Herman (1989), Merz-Prieβ & Riding (1999) and Lu *et al.* (2000) who have all reported examples of tufa-depositing groundwaters conforming to a similar sequence of chemical changes. The deposition of tufa is driven by the degassing of CO_2 from supersaturated waters and concentrations of carbonate ions are within the ranges reported by the above workers. Low supersaturation values (SIc < 1.26) indicate that photosynthetic activity does not play a part (Pentecost, 1992). Spatial changes are shown by an increase in the degree of calcite saturation downstream in relation to a decrease in dissolved CO_2 . The decrease in HCO_3^- concentration and increase in pH downstream at both sites reflect the loss of CO_2 along the flow path of the streams.

3.12.1 Interpretation of downstream carbonate chemistry

3.12.1.1 Processes at Whitehole Farm Spring

The results of the hydrogeochemical analysis of Whitehole Farm Spring with respect to the general pattern of the carbonate system parameters, can be described in the following way:

Precipitation and surface water from the catchment containing H_2CO_3, dissolved solids, suspended sediment and organic material enters the sinkhole at Pitten St. and travels underground through a closed system of fractures and fissures in the limestone (Chapter 2). A certain amount of filtration, adsorption and ion exchange takes place within the fissures which are representative of immature karst (Ford & Williams 1989). The aggressive water dissolves the limestone ($CaCO_3$) during its subterranean passage. Ca^{2+}, HCO_3^- and CO_2 pass into solution. When the water reaches the resurgence at Whitehole Farm Spring the system becomes open. The springwater, containing high concentrations of CO_2 enters the settling tank (Fig. 10) then degasses on its exit at the tank overflow (Fig. 11), in response to the disequilibrium between the spring water and the atmosphere. The pH and SIc of the resurgence water is initially low and the water at this stage is undersaturated with respect to calcite but Ca^{2+}, CO_3^{2-} and HCO_3^- levels in solution are high. The temperature of the water increases slightly as it travels downstream over the irregular and rocky stream bed and further degassing of

CO_2 takes place along the flowpath. Turbulent flow ocurs at the small cascades and terraces and through contact with organic matter within the stream flow. Laminar flow takes place in the small pools behind the debris dams and terraces. Dissolved oxygen enters the water at the areas of turbulent flow i.e. the cascades, and the pH rises as CO_2 is lost from the water. The SIc increases to supersaturation levels. At approximately 100 metres downstream the nucleation of calcite takes place heterogeneously in contact with compatible surfaces within the stream such as pre-existing tufa/calcite, limestone rocks and organic matter (Fig.12). Ca^{2+} and HCO_3^- levels decrease as precipitation of tufa takes place. The water then returns to equilibrium with respect to calcite. Although degassing has taken place, the stream remains supersaturated with CO_2 and continues to degas to the atmosphere. Tufa deposition continues downstream to the confluence with the River Mells.

3.12.1.2 Processes at St. Dunstan's Well.

In general the processes at St. Dunstan's Well are similar to those at Whitehole Farm Spring and can be described in the following way: Precipitation and surface water containing H_2CO_3, dissolved solids, suspended sediment and organic material from the catchment enter the sinkhole at Withybrook and travels underground initially through a closed system of fissures and fractures. The aggressive water dissolves the limestone putting Ca^{2+}, HCO_3^- and CO_3 into solution. Some filtration, adsorption and ion exchange takes place before the water passes into a more open system of large conduits and cave passages before it reaches the resurgence. As the water reaches the open passages CO_2 begins to degas to the cave atmosphere and turbulent flow occurs over the rocky floor. This causes $CaCO_3$ to precipitate within the caves and nucleates in contact with the compatible mineral lattice of the limestone and forms as spelaeothem which, in turn, is a suitable nucleation site for further heterogeneous nucleation. The water resurges at St. Dunstan's Well (Fig. 7), still supersaturated with CO_2, but with lowered amounts of Ca, HCO_3 and CO_3. As the water travels downstream, more degassing of CO_2 takes place, particularly at the waterfall and weir but the rest of the stream has a relatively deep, laminar flow through the constructed channel (Fig. 9). After the waterfall, Ca levels increase slightly. This particular reaction differs from the sequence described for Whitehole Farm Spring and those reported by previous authors, for example, Merz-Prieβ & Riding (1999), where Ca was shown to decline downstream. The increase in calcium could be a result of dissolution of the man-made limestone waterfall. However, pH rises and HCO_3 and CO_3 decrease whilst the SIc remains at a similar level to the rising. The combination of high flow, unstable stream bed and modifications to the stream channel means that there is no accumulated inorganic or organic debris in the stream to act as nucleation sites for tufa (Suarez, 1983). The evidence suggests that the stream's natural environment and biota may be a critical factor in the non-deposition of tufa at St. Dunstan's Well.

CHAPTER 4

THE SPRING ECOSYSTEM AND ITS INFLUENCE ON THE DEPOSITION AND MORPHOLOGY OF TUFA

4.1 THE HYDROLOGICAL CHARACTERISTICS OF SPRINGS

Flowing, freshwater environments such as springs, streams and rivers are referred to as lotic systems (Townsend, 1980). They are characterised by their continuous and rapid throughput of water and other materials (Allan & Flecker, 1993). Dynamic interactions between the components of a unidirectional lotic system operate over a range of spatial and temporal scales, within and beyond the channel boundaries (Giller & Malmqvist, 1999). Fluctuations and seasonal changes in flow and water chemistry are common but no two streams have exactly the same species composition or physicochemical conditions (Cummins *et al.*, 1984).

Todd (1980, p. 47) defined a spring as "a concentrated discharge of groundwater appearing at the ground surface as a current of flowing water". In general, where springs are fed by slow seepage through fine materials the flow, water chemistry and temperature remain fairly constant. One of the unique and biologically important features of this type of spring is the temperature of the water which varies little throughout the year (Van der Kamp, 1995). Conversely, springs fed mainly by rapid flow through enlarged openings in the rock, such as those draining karst aquifers are subject to periodic fluctuations in discharge and temperature with variable levels of nutrients and sediment (Bonacci, 1993). This can have adverse effects on the flora and fauna of the stream ecosystem, but from a hydrobiological perspective, the most important factor relating to the flow of a spring is its permanence or persistence (Castella *et al.*, 1995; Smith *et al.*, 2001). Perennial springs discharge throughout the year, whereas intermittent springs discharge only when sufficient groundwater is recharged to maintain flow (Todd, 1980). Extremely low flows in groundwater-dominated streams can be caused by a lack of winter rainfall (Bickerton *et al.* 1993). Nutrients are often low at the headwaters of natural springs, but downstream changes in water chemistry can alter the quantity and quality of the biota, for example, high calcium, hard water springs, such as those found in the Mells Valley, can be high in DO_2, SO_4 and CO_3, but low in N and P (Prescott, 1969). Springs that exhibit a fluctuating discharge not related to rainfall or seasonal effects are classified as periodic springs (Todd, 1980). Intermittent, temporary or ephemeral springs are common in both arid and Mediterranean climates where the stream bed can dry up for more than three months (Giller & Malmqvist, 1999). Ephemeral springs also occur in the East Mendip study area (pers. obs.). Wright (2000) described the influence of plant and cyanobacterial communities and the incorporation of organic matter on the morphology of tufa deposits in ephemeral streams in the Kimberley region of Western Australia. The biota of the streams were subject to a variety of environmental conditions. The majority of rainfall in the Kimberley region occurred as a number of heavy downpours between October and March with high rates of evaporation in the dry season. Although the individual plant species were not named, Wright (2000) also reported that enhanced deposition of tufa was always associated with some form of organic material, mainly grasses, mosses and cyanobacteria and that the tufa dams formed by debris on the stream bed were heavily vegetated. This suggests that many organisms were able to survive and adapt to the regularly changing hydrological conditions.

4.2 THE INFLUENCE OF THE CATCHMENT

The continuous input and transport of dissolved and particulate matter in the water is closely linked with the surrounding terrestrial system or catchment (Giller & Malmqvist, 1998). Chemical nutrients enter the stream as dissolved solids or associated with particulates (Likens & Bormann, 1972) which are provided in the greater proportion by allochthonous matter (Fisher & Likens, 1973). On a large scale, the influence of the catchment on the lotic ecosystem was described by Hynes (1975) who stated that climate, underlying geology and vegetation were links in a complex chain of organic and inorganic relationships between and within the stream water, its inhabitants and its environment. Hynes (1975) further concluded that anthropogenic changes in the catchment could have large effects on the stream. The Hubbard Brook Ecosystem Study (Likens & Bormann, 1995) is a long term, catchment-based study of the biogeochemical cycling of energy and matter within a 3160 ha forested valley in New Hampshire, USA. Information and data from over 30 years of research and field study has shown that environmental stress, such as pollution, deforestation or building, can disrupt the functioning of the ecosystem by altering the nutrient flux within it. The ability of the freshwater ecosystem to recover from environmental disturbance has been the subject of a review by Niemi *et al.* (1990) who revealed that the recovery times of aquatic habitats varied from years to decades. Habitat quality has been shown to be of vital importance to the preservation of biodiversity in lotic ecosystems (Allan & Flecker, 1993). Fluctuations in spring flow, for natural and/or anthropogenic reasons, has been suggested by Goudie *et al.* (1993) as a possible explanation for the decline of tufa deposition in Europe. They suggest that discharge variability has a detrimental effect on the mosses and algae which are a main component in the framework of many tufa deposits.

4.3 THE FLORA OF TUFA-DEPOSITING SPRINGS

Organisms such as cyanobacteria and eukaryotic algae have been closely associated with the deposition of calcium carbonate (Pentecost, 1991) but groundwater-dominated streams have certain natural characteristics which can affect the functioning of the aquatic species within them (Petts et al., 1999). Consequently, the species diversity of some springs can be relatively low, as a result of their individual isolation and fluctuating environment (Giller & Malmqvist, 1999).

The flora of many perennial tufa and travertine-depositing springs have been recorded and reported to play a major role in the formation of the deposits with cyanobacteria, eukaryotic algae and bryophytes having the closest associations (Golubić, 1973; Pentecost, 1978; Janssen *et al.*, 1999; Pentecost & Zhang, 2000). Calcicolous mosses such as *Palustriella* (*Cratoneuron*) *commutata* (Hedw.) Roth and *Eucladium verticillatum* are often found in abundance on tufa deposits (Pentecost & Zhaohui, 2002). In a study of fourteen travertine-depositing sites in France and England, the moss species *P. commutata*, in particular, was reported by Pentecost & Zhaohui (2002) to form extensive mats around the springs and kept moist by capillarity rather than by fast-flowing water. Tufa (travertine) was deposited on bare stems at the base of the moss mats. Cyanobacteria and algae tended to become dominant in light-reduced and faster flowing environments (Pentecost, 2003). In a further study by Pentecost & Zhaohui (2006), *Palustriella commutata* was reported to be tolerant of a wide range of environmental and hydrological conditions and was capable of growing in exposed situations.

Purely inorganic tufa deposits appear to be rare (Kempe & Emeis, 1985), and Pentecost (1990a) suggested that the formation of travertine would be unlikely without the presence of algae and bryophytes which remove carbon dioxide from the water during photosynthesis. However, Pentecost (1978) had demonstrated that only 1 – 2% of all precipitated carbonate in freshwater systems was due to algal photosynthesis. The plants can act as substrates and sediment particle traps for the nucleation of calcite crystals (Zhang *et al.* 2001). Pentecost & Zhang (2000), suggested that the growths of lower plants created a stable framework for nucleation of calcite crystals in turbulent water and increased the surface area available as a substrate for the deposition of tufa. Bryophytes associated with travertine deposits can greatly increase the surface area available for the nucleation (Pentecost, 1991). Organic matter such as woody debris and leaf litter from the bankside vegetation can accumulate in the stream throughout the year and also provide substrates for tufa deposition (pers. obs.). Non-living organic matter may strongly influence the deposition of tufa (Trichet & Défarge, 1995). The travertine dams of the Slade Brook in Gloucestershire have developed within mixed woodland and Pentecost *et al.* (2000) suggested that the formation of the dams was assisted by accumulations of woody debris in the stream becoming encrusted with calcium carbonate and subsequently colonised by cyanobacteria and algae.

4.4 CYANOBACTERIA AND ALGAE

4.4.1 Environmental adaptations

Adaptations by the stream flora to the flowing water environment can be both morphological and physiological (Jeffries & Mills, 1990). For example, algal species growing in running water are described by Prescott (1969) as requiring the following qualities:

- Anchorage – attached forms can be epiphytic on plants, epipelic on mud or sand or epilithic on rocks. Lithophilic algae often show preference for certain types of rocks for example calcareous, granitic or sandstone.
- A flexible and resilient thallus – growth habit can be prostrate and encrusting or erect and streaming.
- An ability to assimilate in a medium of rapidly changing chemical composition.

- Adaptation of reproductive habits and structure to stream conditions.

Prescott (1969) also observed that planktonic forms of algae were rarely found in rapidly flowing spring-fed streams.

4.4.2 Mucilage

Cyanobacteria are known to play an active part in the precipitation of calcium carbonate by providing favourable sites for nucleation within or on the extracellular mucilaginous polysaccharide (EPS) (Pentecost & Riding, 1986; Merz-Preiß & Riding, 1999). Carbonate deposition by cyanobacteria has been described by Golubić (1973), Pentecost (1978) and Merz (1992). Pentecost & Riding (1986) defined this process as calcification, distinct from the trapping and binding of particles suspended in the surrounding water. Sheath impregnation is thought to occur in aquatic environments where water movement is slow, whereas sheath encrustation occurs in fast flowing streams (Merz-Preiß & Riding, 1999). The mucilage produced by filamentous species such as the cyanobacterium *Rivularia,* for example, traps particles of sediment which can act as nucleation sites for calcite crystallisation (Pentecost, 1987). The structure of the polysaccharide mucus layer could determine the eventual calcite crystal shape (Stal, 2000). As the mucus is decomposed by heterotrophic bacteria, the bound calcium is released causing local supersaturation and the formation of a micrite layer or crust (Stal, 2000). EPS can be present as a thick envelope of mucilage and/or a gelatinous, extracellular sheath (Whitton & Potts, 2000) which allows the diffusion of substances from the surrounding bulk aqueous solution. The highly adhesive mucilage can be excreted in large quantities as a reaction to physiological stress (Kempe & Emeis, 1985). For example, Ortega-Calvo & Stal (1994) revealed that, under laboratory conditions, the unicellular cyanobacterium *Gloeothece* produced copious mucilage when nitrogen-limited. The mucilage, often pigmented, protects sub-aerial species from the effects of intense UV light and allows the organisms to withstand long periods of desiccation (Prescott, 1969). The mucilage may also prevent the attachment of epiphytes to the cell walls, for example, filamentous macroalgae such as *Zygnema* produce much mucilage and have a sparse epiphytic flora, whereas *Vaucheria* and *Cladophora* filaments have non-mucilaginous rough walls and can become densely coated with epiphytes (Round,1973). Biofilms adhering to surfaces in flowing water consist mainly of bacterial colonies held together by extracellular polysaccharides (Costerton *et al.*, 1995; Howard *et al.* 1999) which can often extend several micrometres from the bacterial cell wall (Bayer & Thurrow, 1997).

4.4.3 Physiological responses

Light is a critical factor in the ecology of freshwater algae because of its role in photosynthesis, reproduction and movement (Round, 1973). Some species are inhibited by intense light and most are unable to adjust to highly illuminated habitats (Prescott, 1969). Cyanobacteria respond to light and are adapted to grow at low light intensities. Excess light can cause damage to the organism (Stal, 2000). Calcium carbonate deposited as spelaeothem, such as stalactites, stalagmites and flowstone which contained cyanobacterial species have been reported to be growing in caves where only small amounts of light are present (Cox *et al.*, 1989).

Algae may move towards or away from light, a process known as phototropism (Round, 1973). Phototaxis is a movement whereby the organism orients itself to the direction of the light and can be either positive or negative i.e. towards or away from the light in order to gain their optimum position (Häder, 1987). Many cyanobacteria are phototactic, positively in low light and negatively in high light intensities (Round, 1973). At intermediate light levels, populations often split into two directions (Stal, 2000). Photokinesis is the speed of movement which increases with light intensity and the greater supply of energy (Round, 1973). Häder (1987) described the photophobic response of cyanobacteria to a sudden change in light intensity when the direction of movement was reversed. As light intensity was decreased, the organisms moved to the area of most remaining light and as light intensity was increased the organisms accumulated in the shade. Some species stopped moving in darkness or at very high fluence rates. The responses were described as step-down and step-up respectively, and a further study by Häder (1988) concluded that the movements were related to photosynthesis. Changes in light intensity and/or direction caused a photophobic response which could be a reversal, a temporary stop or a change in direction and were species specific. The extrusion of mucilage from pores in the algal cell wall and filling the sheath has been suggested as a method of propulsive movement, or motility, for some species of algae (Pankratz & Bowen, 1963) although this was later questioned by Holton & Freeman (1965) who argued that the organism would be unable to produce the large amounts of mucilage needed for gliding. Motile, filamentous algae glide by self propulsion along a surface, which can be the interior of the sheath. The filaments, which consist of one to several trichomes enclosed in a sheath, or trichomes, which are single chains of cells excluding the sheaths (Pentecost, 2003), can move out of the sheath and leave it behind as an empty shell or mould (Bertocchi *et al.*, 1990),. Trichomes may also glide along each other (Stal, 2000). Motility allows photosensitive algae to respond individually to light stimuli and in this way they can escape death from complete encrustation by calcite (Golubić, 1973).

4.5 BIOLOGICAL MINERALISATION

Certain microorganisms in the biosphere can be considered as geological agents as some types of mineral formation, such as tufa, may be the result of active (intracellular deposition) or passive (extracellular adsorption or ion exchange) microbial activity (Ehrlich,1996). A distinction has been made by Lowenstam (1986) between these two types of biological mineralisation; biologically-controlled mineralisation and biologically-induced mineralisation. In the former, the causative organism controls the form and position of the deposited mineral; in the latter, the organism has no control. Biological mineralisation can take place under aerobic or anaerobic conditions. In aerobic mineralisation, organic matter is completely degraded, or oxidised, by microbes unless it contains matter which is difficult to break down, such as lignin in wood (Ehrlich, 1996). It has been suggested by Kobluk & Risk (1977) that bacterial decay may alter the depositional microenvironment in favour of precipitation of calcium carbonate on a non-carbonate organic surface. Bacterial mucilage can provide a site for passive biomineralisation of calcite

(Chafetz & Buczynski, 1992). Other minerals such as iron sulphides and oxides, manganese oxides, calcium carbonate and silica may be produced autogenically by microbes (Lowenstam, 1981). Woodruff *et al.* (1999) reported that microbial and algal biofilms which cover the surfaces of aquatic sediments can create microenvironments that influence the chemical flux across the sediment-water interface. The study concluded that concentrations of solutes varied spatially and temporally and resulted in vertical and horizontal stratification of minerals within the biofilm and underlying sediment. Terrestrial lotic environments such as river and stream beds can become covered with a calcified biofilm or microbial mat (Golubić, 1973). Calcified biofilm can form micrite in layers and envelopes within the deposits (Riding, 2000). Lithification is a geological process where microbes may produce a mineral cement such as calcium carbonate, iron oxide or silicate, which then binds inorganic sediment particles together to form a sedimentary rock (Ehrlich, 1996). Bacteria, including cyanobacteria, have been shown to deposit calcium carbonate both extracellularly and intracellularly (Krumbein, 1974; Morita, 1980; Chafetz & Buczynski, 1992). Chafetz & Folk (1984) discussed the role of bacteria in the formation of carbonate cements and their effects on the morphology and fabric of travertines. Bacteria, commonly straight rods, formed clumps encased by a single calcite crystal. When the bacteria decayed they left an abundance of voids or micropores in a variety of forms within the calcite deposits. Some forms showed a repeated cyclic lamination. Numerous bacterial species have been identified by Freiderich *et al.* (1982) in limestone spring water and cave sediments at locations in the Mendip Hills, including one of the sites in this study namely, St. Dunstan's Well. They also demonstrated that swallet water generally had higher bacterial counts than percolation water. This was considered to be due to the very low filtering capacities and turbulence of conduit flow springs (Atkinson,1977b).

Studies of the marine carbonate environment have shown that bacteria can induce calcification (Krumbein, 1979; Chafetz & Buczynski, 1992). Greenfield (1963) demonstrated that, in nitrogenous media with optimum concentrations of Ca and Mg at the cell surface, a marine pseudomonad bacterium in culture acted as nuclei for the precipitation of calcium carbonate crystals. The species also exhibited calcium-binding properties. However, in a study of a similar bacterial species isolated from ten actively depositing freshwater travertine sites it was revealed by Pentecost & Terry (1988) that none of the bacteria nucleated calcite from calcium bicarbonate solutions. Calcite deposition by anaerobic bacteria was considered to be insignificant because of the naturally oxidising surface environment of the travertines.

Carbonate may also combine with manganese and iron to form natural deposits such as rhodochrosite ($MnCO_3$) and siderite ($FeCO_3$). Siderite, or ferrous carbonate, is common in non-marine, organic-rich mudrocks and forms where carbonate activity in the water is high (Tucker, 1988). The formation of siderite in marine sediments was demonstrated in culture, by Roden & Lovley (1993), to be a direct result of the bacterial reduction of ferric iron (Fe^{3+}) to ferrous iron (Fe^{2+}). Sawicki *et al.* (1995) analysed biofilms on exposed rocks from an underground laboratory in Canada to reveal the presence of siderite in association with bacterial cells. They suggested that the Fe^{2+} was bound to the anionic surfaces of the bacterial cells where it reacted with bicarbonate derived from the decomposition of organic matter. The relative stabilities of Fe^{2+} and Fe^{3+} are such that only small changes in environmental conditions are required to alter the oxidation state (O'Neill, 1994). Iron in solution in river and ground water is in very low concentrations (< 1 mg l^{-1}). In the pH and Eh ranges of most natural surface waters iron is present as the highly insoluble ferric hydroxide ($Fe(OH)_3$) (Tucker, 1988). Microbial respiration during the decomposition of organic matter consumes oxygen and creates anaerobic, reducing conditions within the sediment. In an oxidising and alkaline environment, haematite (Fe_2O_3) can be deposited in the form of micron-sized crystals and has also been associated with individual bacterial cells (Sawicki *et al.*, 1995).

4.6 ALGAL LIMESTONES AND MORPHOLOGIES

Limestones can be defined by a variety of properties such as colour, crystal size, composition and texture or fabric of the rock. The fabric of a tufa deposit is defined by Pentecost & Viles (1994, p.306) as "the architecture of the deposit (i.e. the arrangement, density and size of the building units)" and the deposit can be classified by the predominant types of plants that have been contained within it. Of major importance as the building units of many tufa deposits are the bryophytes and algae and some deposits have been classified in this way. For example, moss tufa would contain a bryophyte species such as *Palustriella commutata* (Emeis *et al.*, 1987; Pentecost, 1987) or an Oscillatoriaceae tufa would be the result of filamentous cyanobacterial colonisation (Irion & Müller, 1968). The growth characteristics of a particular species often determines the gross morphology of the tufa deposit. In flowing water, attached, epilithic algal filaments are horizontally aligned giving a streamlined appearance to the mass e.g. *Vaucheria* tufa, which was first described by Wallner (1934). The lithification of live algae and mosses has also been described by Emig (1917) and Golubić (1969) who suggested that, in order to survive, the rate of upward growth of the organism must exceed the rate of calcification. In the marine coastal environment, structures formed from the calcified assemblages of algae and cyanophytes are commonly known as stromatolites. These carbonate deposits are laminated and often lithified (Stal, 2000). Bathurst (1967) described the ability of the algal communities within the mats to trap fine-grained marine sediments and create a more stable local environment. Freshwater stromatolites share many sedimentological similarities with their marine counterparts, particularly with regard to the role played by filamentous cyanophyte genera such as *Oscillatoria*, *Phormidium, Lyngbya*, *Microcoleus* and *Schizothrix* in the formation of laminated and non-laminated cyanobacterial mats (Golubić, 1973; Stal, 2000). Pedley (1990) described "stromatolitic tufa" as having a close association with Oscillatorian cyanobacteria and often occuring with detrital tufa, which consisted of carbonate encrusted plant fragments and "oncoids" or "oncolites" (Pia, 1933). Roddy (1915) discovered numerous concretions of varying size and shape in a freshwater stream, Connestoga Creek, in Pennsylvania, USA. The concretions were found to have nuclei consisting of either local pebbles or carbonaceous matter which were surrounded by concentric laminae. He also attributed their growth to the presence of cyanophyte species such as *Gleocapsa, Oscillatoria* and *Rivularia* and several species of green algae. Diatoms and desmids were also found to be present on examination of the samples. Iron deposits were present in varying amounts in the samples which Roddy (1915) attributed to bacterial processes. Laminar accretion of carbonate was observed to be thicker on the underside of each concretion.

4.6.1 Tufa morphologies

Tufa precipitated onto organic debris in the stream such as branches, leaves and mosses often becomes colonised by algae and cyanobacteria. The species associated with the deposits influence the morphology and petrology of the tufa and characteristic crystal forms occur in relation to specific organisms and species (Janssen *et al.*, 1999). For example, irregular surfaces on the Slade Brook dams were caused by the growth of the filamentous alga *Vaucheria sessilis* (Vaucher) de Candolle (Pentecost *et al.*, 2000). This species, and also *V. geminata* (Vaucher) de Candolle , was present on the Nash Brook tufa deposits in South Wales where they gave a "spiky" microtopography to the downstream overhang of the dams (Viles & Pentecost, 1999). In areas of more laminar flow, the tufa became more rounded and "nodular" in form and *Vaucheria* was replaced by the cyanobacterium *Phormidium incrustatum* (Nägeli) Gomont. Wallner (1934) described extensive deposits of *Vaucheria* tufa in Paterzell, Bavaria with the strongest active growth of *V. geminata*, in the fast flowing zone of a tufa-depositing stream. Apical lengthening of the partially tufa-encrusted colonies created a characteristic keel-like morphology to the deposits formed by this species growing in the stream current. Wallner (1934) also noted that the *Vaucheria* tufa decreased in sections of the stream where the cyanophyte *Plectonema* was present. The cyanobacteria colonised the growing *Vaucheria* mats from underneath eventually encasing them in a tufa "shell" which consequently changed the inner structure and overall morphology of the tufa deposits. The genus *Plectonema* contains species which are endolithic (Pentecost & Whitton, 2000) i.e rock boring species (Trudgill, 1985). They are known to survive long periods of desiccation (Whitton, 2000) which is a physiological characteristic they have in common with *Vaucheria* (Dunphy *et al.* 2001).

4.7 TUFA MICROSTRUCTURE AND CRYSTALLOGRAPHY

A survey of British tufas and travertines by Pentecost (1993) concluded that most modern spring tufa deposits are forming as carbonate crusts in streams. In a study of Recent (i.e. Holocene) and fossil (pre-Holocene) tufa deposits in Belgium Janssen *et al.* (1999) reported characteristic crystal forms within the tufa in relation to the inorganic and organic substrates of the deposits. Scanning electron microscope (SEM) examination revealed that laminated carbonate crusts from the river bed differed from deposits formed around organic substrates by containing only cyanobacterial filaments of the species *Phormidium incrustatum* Gomont (1889). There was no evidence of moss or other plants within the samples. On artificial substrates such as glass slides, calcite precipitation only commenced after colonisation of the slides by algae.

No calcite precipitation was found on copper plates due to the toxicity of copper for micro-organisms (Huntsman & Sunda, 1980). The results were similar to those of Kempe & Emeis (1985) and Emeis *et al.* (1987) who also used artificial substrates in their study of calcite deposition in the Plitvice Lakes. They suggested that high calcium concentrations stimulated the secretion of adhesive mucus by epiphytic diatoms and cyanobacteria. Micrite crystals trapped in the mucus acted as seeds for heterogenous calcite precipitation. Kano *et al.* (2003) investigated the origin of laminated tufa deposits in a cold, freshwater stream in Japan using a variety of techniques. Samples were collected from the stream, which was situated within cedar woodland. The shaded tufa surfaces were covered with moss, algae and cyanobacteria, the most abundant cyanobacterial genera being *Phormidium, Lyngbya* and *Symploca*. Thin section examination of the samples revealed alternations of porous and dense laminae which were shown under SEM to be layers of rhombohedral calcite (sparite) crystals and micrite. The dense, micritic laminae were associated with encrusted cyanobacterial filaments 5-10 µm in diameter. The more porous sparite crystals encrusted filaments 15-30 µm in diameter. The orientation of the filaments was perpendicular to the lamina boundary. The laminations displayed a seasonal pattern with the dense layers having been deposited in summer and early autumn and the porous layers deposited in winter and spring. The investigation also revealed large pores occuring in the upper layers of the tufa which were enveloped by a micritic fringe. Kano *et al.* (2003) suggested that they were the remains of Trichopteran (caddis-fly) larval galleries, or retreats. The larvae build conspicuous portable or anchored retreats made from organic or inorganic fragments from the stream bed held together with silk produced by their salivary glands (Brönmark and Hansson, 1999). The species of the genus *Hydropsyche* live in rapidly flowing streams and spin nets into which food is swept (Clegg, 1985). Drysdale (1999) considered that caddis-fly larvae of the genus *Cheumatopsyche* enhanced travertine deposition rates from two to 20 times by their modification of the microenvironment. The introduction of materials for retreat building and the production of silken nets increased the microtopographic relief and surface area available for precipitation of calcium carbonate. The encrusted retreats and nets also increased the porosity of the travertine fabric.

The observation of cyclical changes in the size of the calcite crystals was reported by Chafetz & Folk (1984) who also discovered microscopic laminations and shrub-like forms within the major layers of hot spring travertines. They attributed the variations in microstructure to the calcification of living photosynthetic bacteria. However, it was argued by Pentecost (1990b) in his study of travertine shrubs that inorganic processes such as the rapid degassing of calcium bicarbonate-rich water were responsible for the formation of the dendritic crystal growth patterns. Examination of thin sections by Irion & Müller (1968) revealed the influence of lower plants on the fabric of tufa samples collected from the Schwäbische Alb, Germany. More than 99% of the deposited crystals were calcite with small amounts of other minerals, such as quartz, occuring in cavities in the tufa. By this method they were able to determine that the tufa fabric was either algal, moss or inorganic calcareous sinter. The algal tufa was identified as either Cyanophyceae, probably *Oscillatoria*, *Schizothrix,* or *Vaucheria*. The Oscillatoriaceae tufa exhibited well developed seasonal growth layers or laminae.

4.8 AIM

The aim of this sedtion of the thesis was to examine the flora of the two study springs and to determine whether the observed species influence the deposition and morphology of the tufa deposits at Whitehole Farm Spring. This would be achieved by:

i) Making field observations of the ecology of lower plants growing in the two study springs and their streams.

ii) Sampling and identifying algae and cyanobacteria from each water sampling point.

iii) Collecting and examining samples of newly accreted tufa by means of artificial substrates.

iv) Examining samples of natural tufa from Whitehole Farm Spring using biological and geological laboratory techniques .

4.9 METHODS

4.9.1 Field methods

Observations on the stream flora were made at the two study sites, Whitehole Farm Spring and St. Dunstan's Well, during May 2002 and October 2002 by walking the length of the stream channels of both springs. Observations on the stream flora at both sites were made throughout the study period. At both upper and lower sampling points at the springs, visible growths of epilithic algae and/or cyanobacteria were collected by scraping the rocks into a plankton net before transferring the material to a labelled sample bottle. Bryophytes and macrophytes were collected by hand and placed in plastic bags with a small amount of stream water. Submerged organic debris such as twigs and leaves were also collected and placed in plastic bags. In order to collect samples of newly accreted tufa, artificial substrates were made by bolting six wooden splints (tongue depressors) to a solid wooden base (Fig. 25). A 1 cm gap was left between each of the splints and the base by means of a stainless steel nut placed between the splints and the base to allow accretion on the undersurface. The apparatus was placed in the main stream flow at the tufa-depositing section of Whitehole Farm Spring and held in position by placing two rocks on either side of the base (Fig. 26). A similar apparatus was placed in the stream at the lower sampling point at St. Dunstan's Well. The substrates were left in the two streams for eight months from October 2002 to June 2003.

During May 2003, specimens of loose, older tufa and oncoids were picked up from the stream bed at Whitehole Farm Spring and surface samples were removed using a sharp wood chisel. The samples were transported to the laboratory in sealed plastic bags containing a small quantity of stream water. All samples were stored in an environmental cabinet at 8°C day neutral (i.e. 12 hrs light :12 hrs dark cycle) and examined under the light microscope within three days. Live algae were identified to genus, and where possible, to species level using the taxonomic text by John *et al.* (2002).

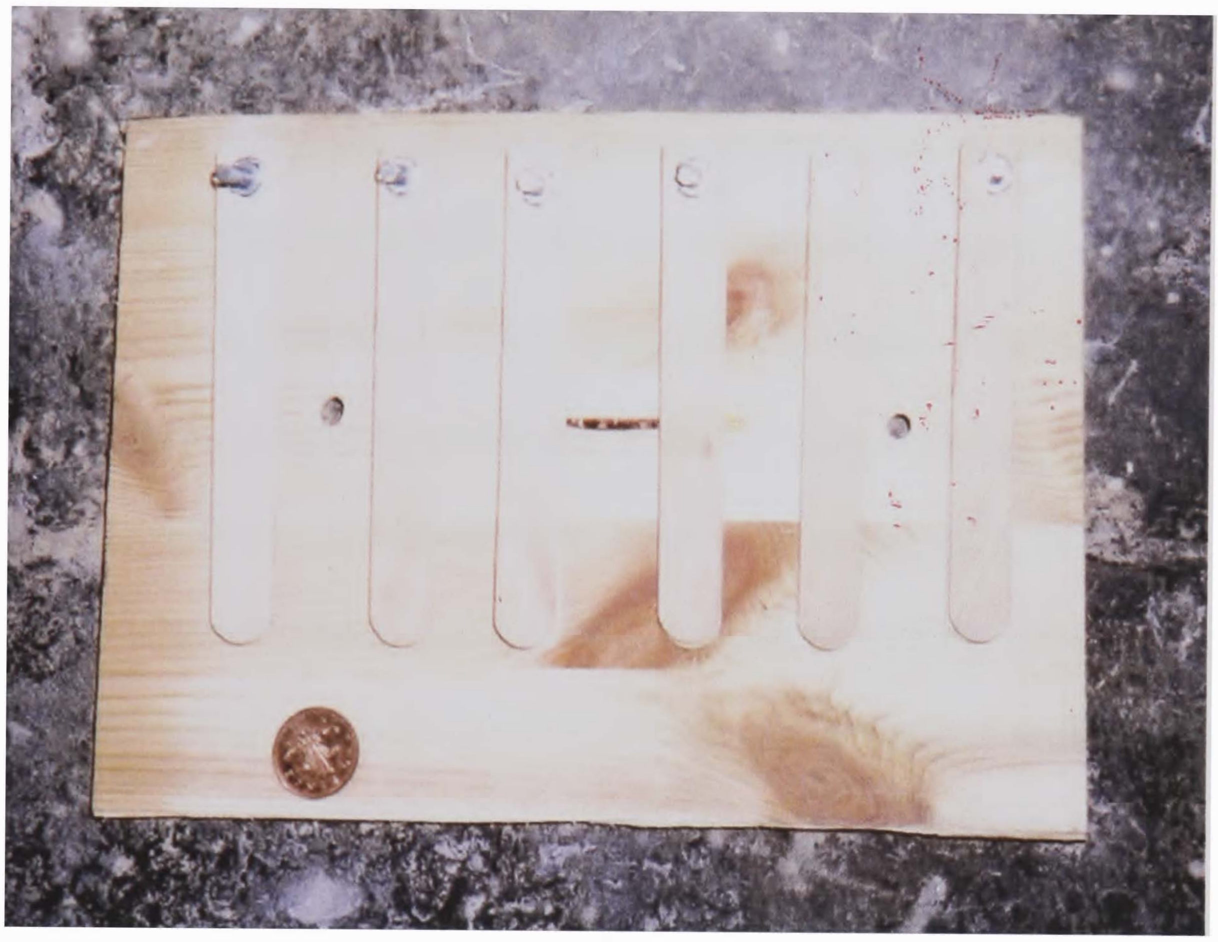


Fig. 25. Apparatus constructed for in-stream tufa accretion tests.

Fig. 26. Apparatus shown in Fig. 25 in place at Whitehole Farm Spring.

4.9.2 Laboratory methods

In the laboratory, the tufa samples were prepared for petrological examination under the light microscope using an acetate peel technique (Joy & Willis 1956; Katz & Friedman 1965; Davies & Till 1968). This method was used as most of the samples were found to be too fragile during the grinding process for conventional thin-sectioning, even after embedding with resin. The preparation of geological thin sections (slices of rock, ground and polished to a thickness of approximately 0.03 mm) is a technique which allows the almost transparent samples to be examined by microscopy using transmitted light. In this study, the peel method was used in combination with embedding techniques using a clear, hydrophilic, low-viscosity acrylic resin L.R. White (Hard Grade) manufactured by the London Resin Company. The resin was supplied by Agar Scientific Ltd., Essex and was recommended by them for use in microtomy and the "sawing and grinding" of calcified tissues.

4.9.3 Preparation of samples

All tufa samples were fully air-dried in the laboratory before transferring into either (i) aluminium foil moulds and plastic ice cube trays for cellulose peels or (ii) small polyethylene embedding capsules (Agar Scientific Ltd.) for microtomy, depending on the size of the sample. Larger samples of older tufa were prepared in the following way by cold curing.

Prior to transferring the dry samples, the bases of the moulds were smeared with accelerator applied using a cotton bud. Accelerator was then added to the resin at a rate of 1 drop per 15 ml resin and mixed thoroughly. The samples were placed in the moulds and the resin mixture poured over them until the tufa had fully absorbed the resin. More resin was then added to cover the samples completely. The filled moulds were then transferred to a vacuum dessicator where vacuum was applied for 20 minutes at room temperature to remove air bubbles from the resin. In order to avoid heat cracking of the sample or matrix, the moulds were stood in iced water in the dessicator as the temperature rose. Hardening was complete in 20 – 25 minutes and the embedded blocks were removed from the moulds. Without the use of a hardener, the process can take between 7 and 10 days at room temperature. Excess resin was removed by trimming the blocks on a diamond saw which was also used to cut sections of the samples in the required orientation.

To prepare the block for making stained peels, the cut surface was ground by hand on a glass plate using a series of carborundum grit sizes from 60 μm down to 12 μm in a distilled water slurry (Adams *et al.* 1984). The section and glass plate were washed clean with water before using the next grade of grit and the section was finally polished with 0.8 μm cerium oxide powder.

Small, air-dried samples of newly accreted tufa and moss fragments were placed in individual, flat-ended polyethylene capsules, 8 mm diameter x 15 mm long for thermal curing. The capsules were then filled to the top with L.R. White resin and capped to exclude oxygen. The filled capsules were then placed upright on a metal tray in an oven for 24 hours at 60°C ± 2°C for polymerization. When cold, the embedded samples were removed by cutting the capsules open with a scalpel or razor blade. The blocks were sectioned to 10 µm thickness on a Reichert Ultracut OM–U3 microtome using laboratory-made glass knives. The sections were picked up and placed on a glass slide using tweezers with extra-fine tips (0.04 mm thickness) and floated out on a hot plate at 60°C with a solution of Mayer's Albumen as an adhesive (Purvis *et al.*,1969). The slides were allowed to dry for 30 minutes before etching and staining.

4.9.4. Etching

Etching can be carried out at any stage in the preparation of samples (Folk, 1959). If the samples are well consolidated or indurated, they can be etched without being embedded although they must first be sawn and ground to a flat surface. Etching also removes loose powder produced from grinding and polishing the surface of the samples which can cause uneven adherence of the acetate film to the sample surface. The prepared flat surface of the sample was immersed in a watch glass containing 2 ml of 0.1M HCl for 10-15 seconds. If the sample was embedded in resin the immersion time was extended to 30 seconds. If the sample was not being stained it was viewed under the stereo microscope after removing surplus acid with deionised water and allowing to air dry.

4.9.5 Staining methodology

The staining methods used in this section for the identification of hard rock minerals, were based on methods by Friedman (1959), Dickson (1965, 1966) and Lindholm and Finkelman (1972). These methods were reported by

Friedman (1971) as being particularly useful for the identification of carbonate minerals under the light microscope. Carbonate minerals such as calcite, aragonite and dolomite are difficult to identify in hand specimens and under the petrological microscope because their physical characteristics are similar (Friedman, 1959). It is also possible to identify ferrous iron inclusions by these staining methods (Evamy,1963). The period of immersion in the staining solutions varies with the composition, grain size and porosity of the samples.

The colour intensity of the stained sample indicates the density of the crystalline material as fine-grained carbonate fabrics react more rapidly with acid and show deeper colours than coarser fabrics of the same composition because the acid attacks the crystal boundaries. Larger crystals of sparite may appear lightly stained or unstained because of their orientation along the optical axis, where fewest cleavages intersect the polished surface of the sample (Adams & MacKenzie, 2001). The eveness of colour and the depth of red stain indicates the distribution and size of calcite crystal grains. An even distribution of grain sizes and depth of colour would suggest inorganic precipitation, whereas uneven distrubution of colour would indicate a variety of grain sizes and biogenic precipitation. Stain was also applied to sectioned, unembedded samples of indurated tufa and travertine for examination under the low-power stereo microscope. The stereo microscope was used for examination of the stained and unstained surfaces of the newly deposited tufa accretion tests and the distribution of insoluble particles was revealed by etching.

4.9.6 Staining

Three stains were used, individually and in combination, for the identification of minerals in the prepared tufa samples.

1) Alizarin Red S (ARS) (sodium alizarin sulphonate) is an acid stain that was used to distinguish calcite from dolomite and to differentiate between slightly different types of calcite such as organic remains and the rock matrix by the intensity of colour imparted on the components. The colour intensity from pale pink to deep pink is affected by the optical orientation of the crystal and the rate of reaction to the stain along the crystal axis (Dickson, 1966). To prepare the stain, 0.1 g ARS was dissolved in 100 ml of 1.5% HCl and stored in a clear glass, stoppered bottle. With the addition of 30% sodium hydroxide (NaOH) to the ARS and boiling the mixture, siderite, or ferrous carbonate, ($FeCO_3$) will stain dark brown to black in the hot solution (Warne, 1962).

2) Potassium ferricyanide, an acid stain, was used individually as a routine analytical test for iron (Warne, 1962). However, carbonate rocks frequently contain small amounts of FeO in the form of ferroan calcite and ferroan dolomite. Potassium ferricyanide was combined with ARS to determine, by colour, iron-free and ferroan compounds within the rock. Preparation of the stain depends on its use:

a) for staining ferrous iron, 5.0 g potassium ferricyanide was dissolved in 20 ml deionised water and 2 ml concentrated HCl. The solution was then diluted to 1000 ml with deionised water (Friedman, 1971).

b) for staining ferroan iron, the solution was prepared by dissolving 1 g ARS and 5 g potassium ferricyanide in 1000 ml of 0.2% HCl (998 ml deionised water with 2 ml concentrated HCl) (Lindholm & Finkelman, 1972).

3) Methylene Blue, a basic stain more frequently used for the differentiation of biological materials, has an affinity for acid tissues (Purvis *et al.*, 1969). Methylene blue in aqueous solution stains the sheaths of many algal and cyanobacterial species (Bold, 1957). It was been found to be of use in this study in the identification of diatoms and organic matter as it does not stain $CaCO_3$. To prepare the stain, 1% aqueous stock solution was made up by dissolving 1.0 g of methylene blue in 99 ml of warm water (50°C). The solution was then filtered and stored in a stoppered bottle.

Fig. 27 shows the minerals which can be identified by staining tufa samples using the solutions described above. The polished surface of the prepared tufa samples was partially immersed in a petri dish containing solutions a-d for 10 minutes. The sample was lifted occasionally to allow gas bubbles to escape. The sample was then removed from the dish and surplus stain washed off with distilled water. The stained sample was allowed to air dry for a few minutes. The dried sample was then pressed, stained surface uppermost, into a piece of plasticine to hold it in position for application of the acetate film (25 μm cellulose acetate replicating tape supplied by Agar Scientific Ltd.) which was cut to the size of the stained surface plus a minimum 1 cm overlap. The surface of the sample was flooded with acetone from a dropper bottle and the acetate film was immediately applied with even pressure to remove air bubbles. The sample and film were left to dry for 20 minutes after which the acetate film was carefully and slowly peeled from the stained surface by handling the overlap. Excess film was trimmed away from the imprinted peel which was then mounted between two microscope slides and bound together with cellotape for examination under the light microscope. All photographs and photomicrographs were taken with a hand-held Nikon Coolpix 4300 digital camera.

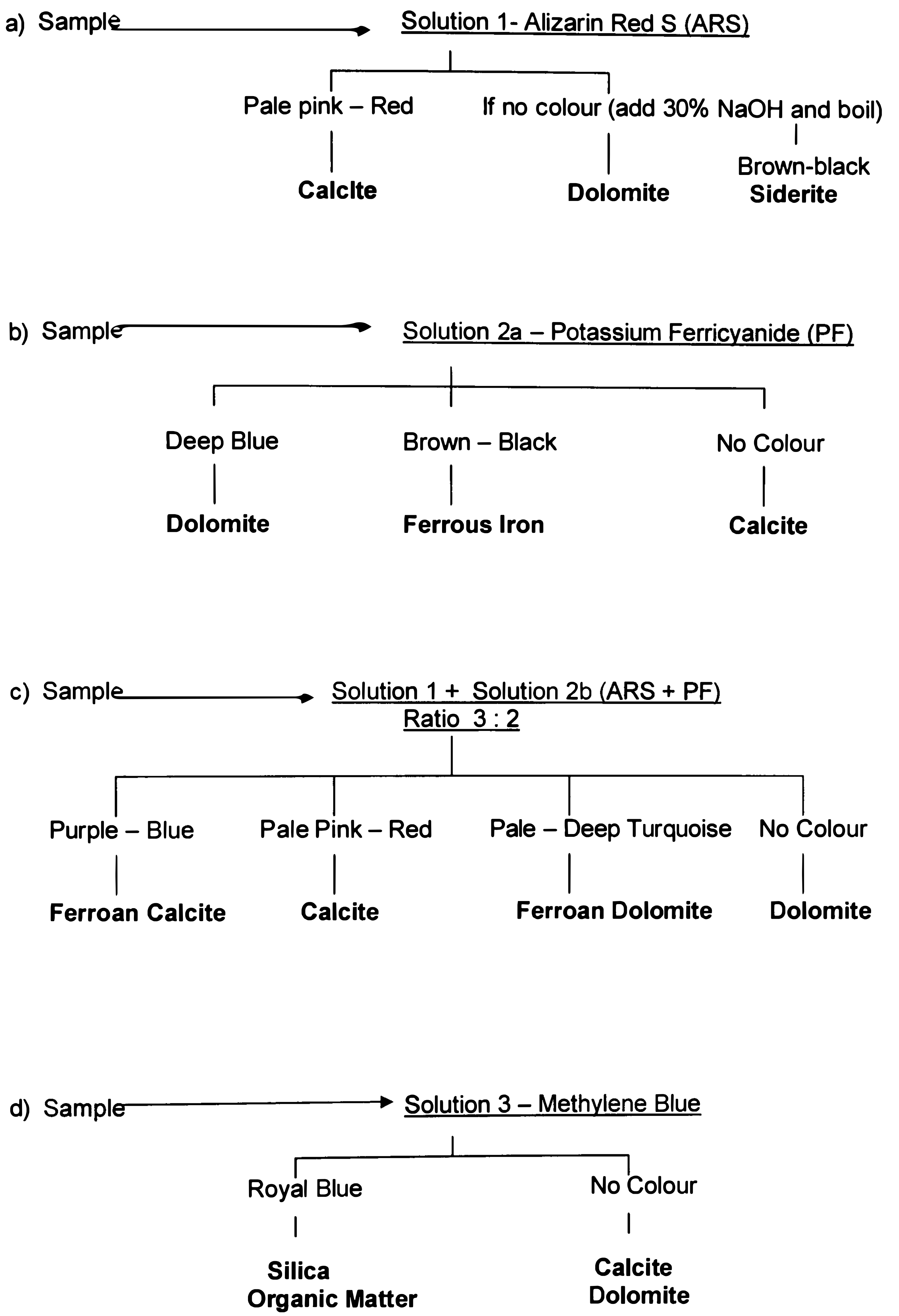


Fig. 27. Flow-chart for the identification of minerals in stained tufa samples

4.10 RESULTS

4.10.1 Field observations

The flora of the study springs and their streams consisted chiefly of bryophytes, cyanobacteria, diatoms, red algae and filamentous green algae, but there were observed differences in species abundance and diversity. Whitehole Farm Spring was heavily vegetated with algae, bryophytes and other terrestrial and aquatic plants throughout its stream course whereas St. Dunstan's Well was colonised by only a few species of algae and bryophytes near the rising. The dominant species at the Whitehole Farm Spring rising was the red alga *Hildenbrandia rivularis* (Liebm.) J.Agardh, which covered many of the Quartzitic Sandstone rocks in the stream bed at the rising (Fig. 28) and for approximately 10 metres downstream. The species was not associated with the tufa deposits and only grew in heavily shaded conditions at the spring rising. *Hildenbrandia* was not present at any point in the stream at St. Dunstan's Well where the dominant algal species was *Cladophora glomerata* (L.) Kütz which was growing attached to submerged rocks 5 metres downstream from the rising (Fig. 29). Colonies of *Vaucheria* were found within the *Cladophora* masses at St. Dunstan's Well. Diatoms were present as epiphytes on the *Vaucheria* and there were epiphytic growths of filamentous cyanobacteria on the *Cladophora*. No other species of algae were observed at St. Dunstan's Well during the study period and other aquatic vegetation was sparse. However, mosses and liverworts were growing on the banks and on submerged rocks at the rising and colonising the walls of the constructed channel downstream. Microscopic examination of samples

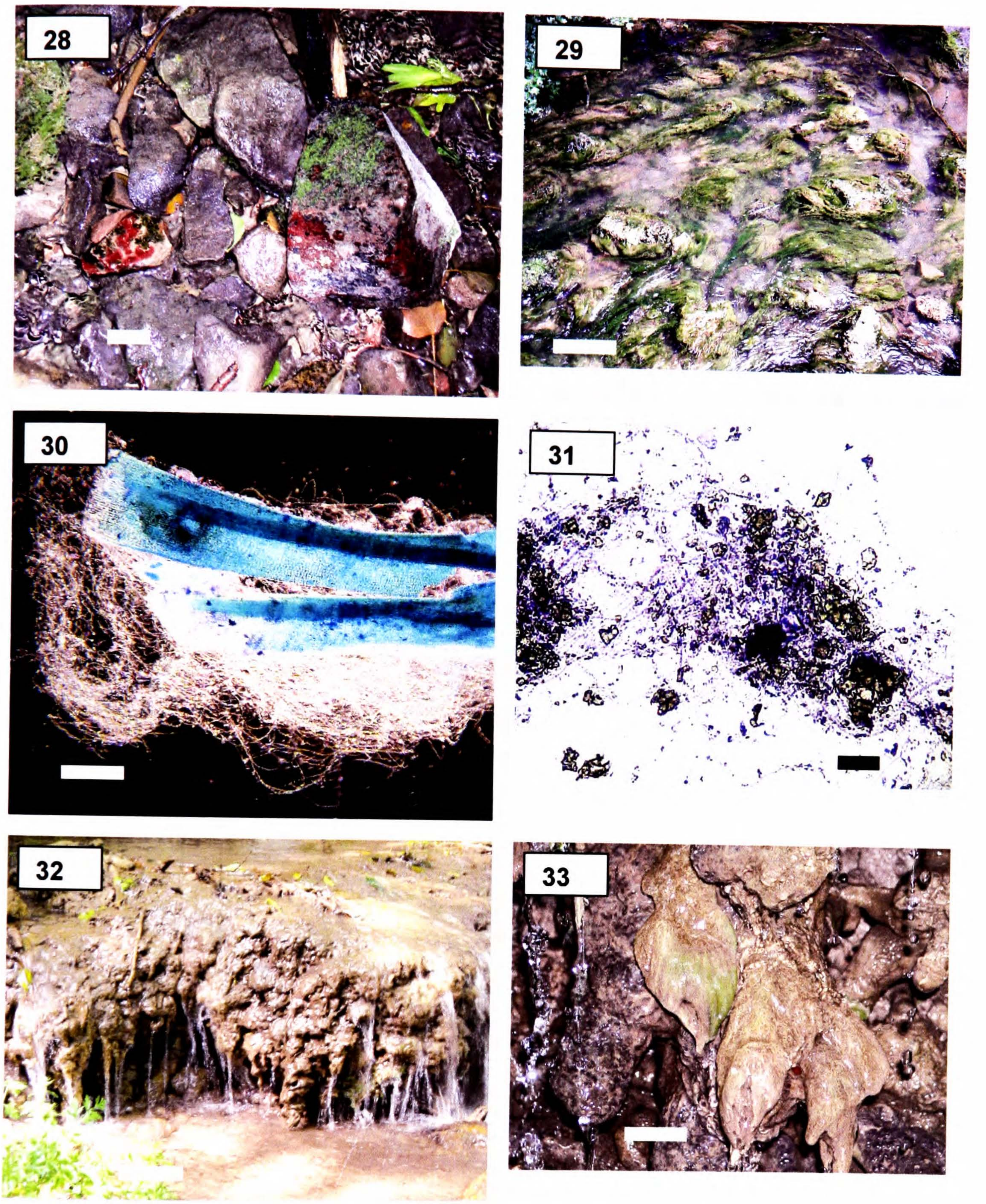


Fig. 28. *Hildenbrandia rivularis* at WHF spring rising (bar=10mm). **Fig. 29**. *Cladophora glomerata* at STDW spring rising (bar=25mm). **Fig. 30**. Cyanobacterial filaments around the base of moss leaves at STDW rising (bar=100µm). **Fig. 31**. Mineral grains and clay particles trapped in cyanobacterial filaments (bar=100µm). **Fig. 32**. *Vaucheria* tufa on lower edges of tufa terraces at WHF (bar=15cm). **Fig. 33**. Growths of *Vaucheria* showing encrustation with tufa and cyanobacterial colonies (bar=5cm).

revealed tangled masses of filamentous cyanobacteria around the plants (Fig. 30) similar to those growing epiphytically on *Cladophora*. The filaments contained numerous trapped sediment particles which were identified as mineral grains, mainly calcite, quartz and clay sediment (Fig. 31). Precise identification of the cyanobacterial species was not possible but using information from the taxonomic text by John *et al.* (2002) it is probable that they were *Lyngbya kuetzingii* Schmidle.

Cladophora glomerata was not present at Whitehole Farm Spring. However, the species was present in the surface stream at Pitten St. which supplies recharge water for the spring where it also contained colonies of *Vaucheria* (pers. obs.). A number of *Vaucheria* species were also found at Whitehole Farm Spring where it was the most abundant macroalgae. All growths of *Vaucheria* were located on the downstream edges of the small tufa terraces (Fig. 32). The *Vaucheria* growing directly within the flow of the stream exhibited the characteristic growth forms described by Wallner (1934) and Pentecost *et al.* (2000).

Vaucheria colonies were most abundant during the spring and summer but became completely encrusted with tufa by late summer and autumn. Dark blue/grey colonies of *Phormidium incrustatum* were visible on tufa beneath the *Vaucheria* deposits (Fig. 33). A substantial amount of the tufa deposits at Whitehole Farm Spring appeared to be formed by the growth and subsequent calcification of *Vaucheria*. Colonies of the green filamentous alga *Zygnema stellinum* (Vaucher) C.Agardh em. Czurda, were found in some of the smaller, more open pools at the edges of the stream where water flow was laminar and calm. No *Zygnema* species were found at St. Dunstan's Well. No planktonic species were found at either spring. The most abundant growths of moss were seen at the lower sampling point B at Whitehole Farm Spring on the small tufa terraces and cascades (Fig. 34). The moss species *Palustriella commutata*, was dominant in the splash zones of the cascades. The species was not present at St. Dunstan's Well. There was much accumulated organic matter such as branches, leaves and seeds along the stream bed at Whitehole Farm Spring. The debris contributed to the formation of the terraces which were encrusted with tufa and colonies of cyanobacteria. Detrital tufa and oncoids were found in the pools behind the small dams. At St. Dunstan's Well there was no organic debris at any point on the stream bed. Many of the stones in the stream channel at Whitehole Farm Spring were covered with the galleries of Trichoptera larvae, whereas none were found at St. Dunstan's Well.

4.10.2 Microscopic observations

Several different morphological types of tufa were present in the Whitehole Farm Spring stream including moss tufa, algal tufa, lithified stream crusts, oncoids and detrital tufa. The moss formed a fragile, open framework for tufa accretion around the base of stems and leaves of the plants (Fig. 35). Tufa forming on and around the *Vaucheria* was also very friable and porous. Tufa had formed on the artificial substrates at Whitehole Farm Spring. The newly accreted tufa on the artificial substrates was very friable and porous. Tufa accretion was thicker (6 mm) on the underside of the substrates than on the upper surface (2 mm). No tufa had accreted on the artificial substrates at St. Dunstan's Well. The tufa oncoid samples (Fig. 36) were less porous and comparatively dense and hard. They varied in size from approximately 5 mm, which could be classed as a pisoid or pisolite (Tucker, 1988), to 60 mm in diameter and spherical/sub-spherical to ellipsoidal in shape. The detrital tufa was variable in texture and shaped according to the organic or inorganic matter on which the tufa had accreted. The morphology of the samples varied. Oncoids, detrital tufa and tufa deposited on the artificial substrates had distinctly different upper and lower surface morphologies. The upper surfaces of the accretion tests exhibited a characteristic, nodular texture (Fig. 37). This was the most common surface texture and was also present on the base of the moss stems, detrital tufa and oncoids and when fresh samples were stained with Methylene Blue, colonies of filamentous cyanobacteria became apparent (Fig. 38). The light-limited under-surfaces of the accretion tests were flatter but with the same nodular texture (Fig. 39). The surfaces of the carbonate crusts sampled from the stream banks were non-porous and smooth with no moss or algal growths (Fig. 40). When the samples were sectioned the inner fabrics ranged from highly porous and friable to dense and lithified, with varying amounts of visible, undecayed organic matter in the form of twigs, leaves and seeds incorporated either as central nuclei or as an inner or surface layer. The majority of calcite had precipitated on organic substrates such as moss, algae and plant parts which would eventually decay. The organic nuclei for the lithified samples were no longer present but were represented in some samples by tiny holes in the centre of a series of compressed concentric rings (Fig. 41).

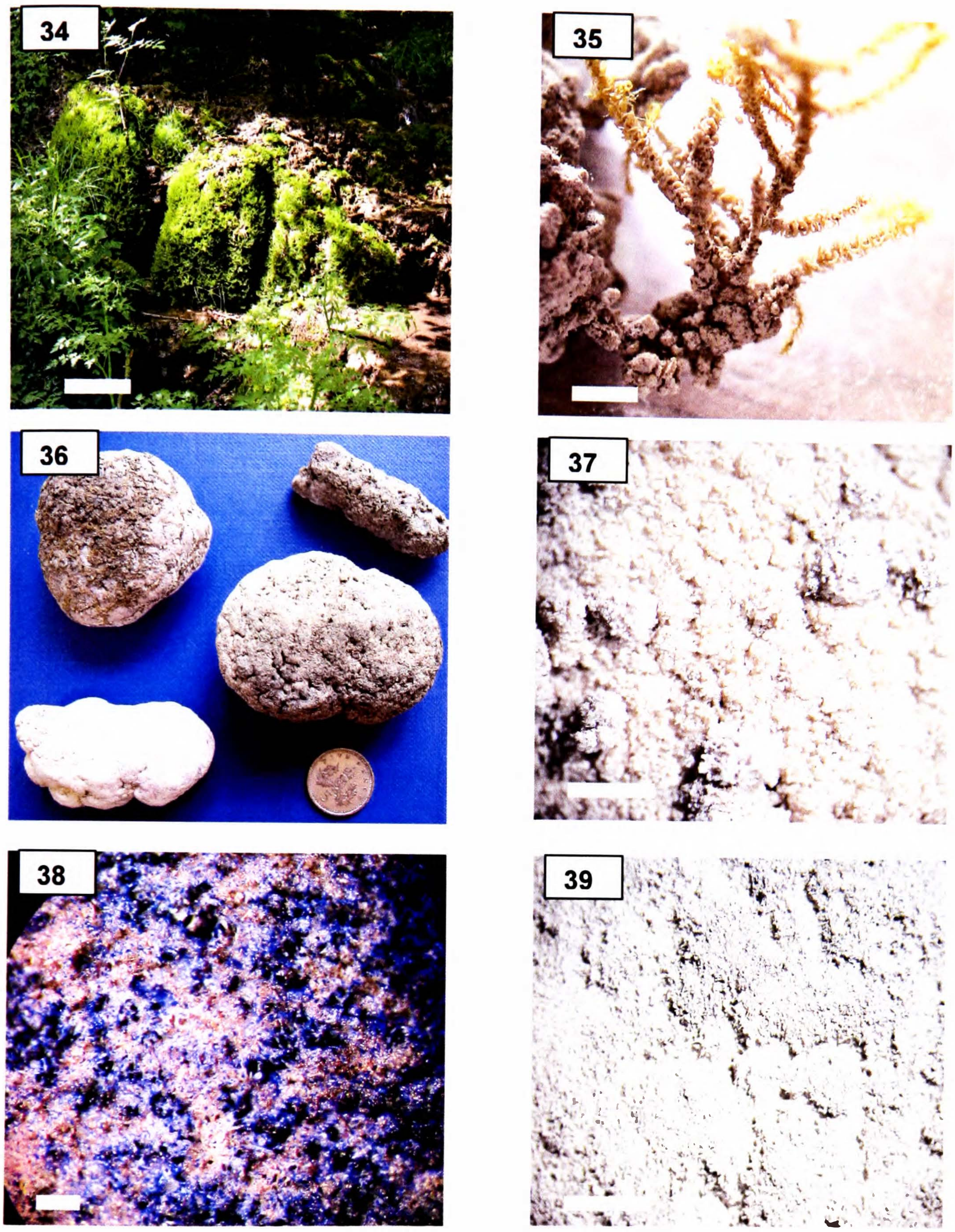


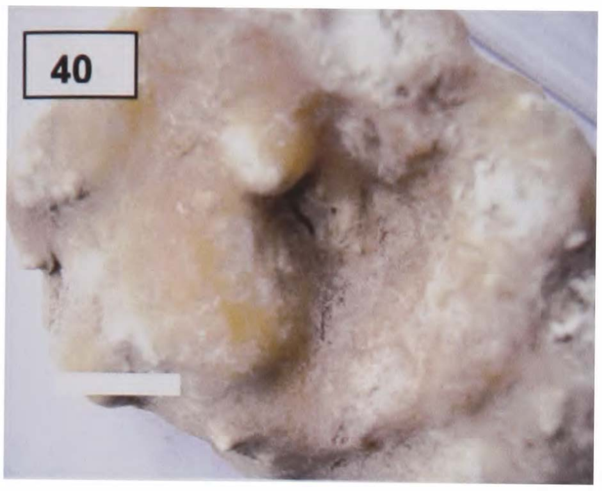
Fig. 34. Moss growths on cascades (bar=30cm). **Fig. 35**. Tufa formed around moss stems (bar=10mm). **Fig. 36.** Tufa oncoids (5p coin scale). **Fig. 37**. Upper surface of newly accreted tufa (bar=1mm) . **Fig. 38**. Upper surface stained with Alizarin Red S and Methylene blue (bar-5mm). **Fig. 39**. Under surface of newly accreted tufa (bar=1mm).

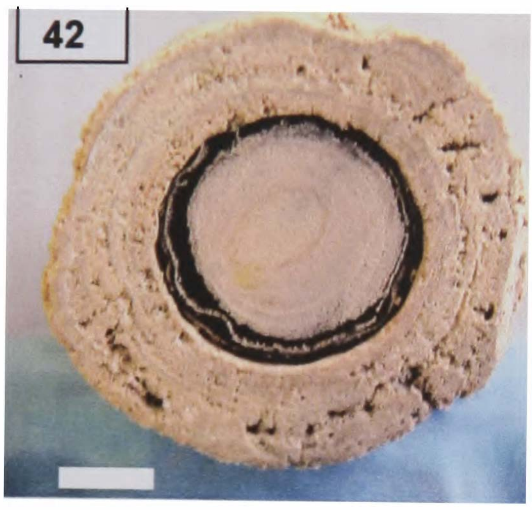
The detrital tufa which had deposited around debris from the surrounding trees contained the undecomposed wood nucleus surrounded by a series of concentric laminae (Fig. 42). The tufa crusts from the stream banks displayed a series of alternating light and dark undulatory, dense laminae, approximately 10 –12 mm thick (Fig. 43). The oncoids (Fig. 36) had a variety of organic and inorganic nuclei including seeds, shells and small pebbles and all nuclei were surrounded by a series of porous, concentric laminae e.g. Fig. 44. The colours of the samples varied from almost white, pale cream, shades of yellow and brown to grey and grey-brown. Some samples of detrital tufa, deposited on the surface of fallen tree branches, were blue/mauve in colour (Fig. 45) and the majority of oncoid samples were blue-grey on the upper surfaces and light grey underneath with a few samples being almost pure white.

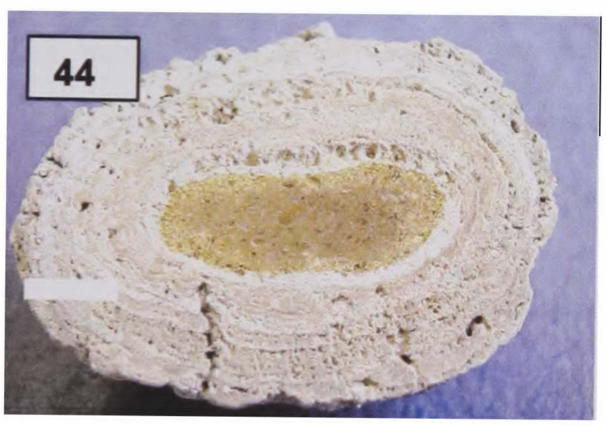
4.10.3 Algal crystal morphology

The morphology of crystals formed around the two main algal species at Whitehole Farm Spring was distinctly different. Individual, well-developed calcite crystals were present on the outer mucilage sheath of *Zygnema* which had been growing in the pools (Fig. 46) whereas anhedral, platy crystals had encrusted *Vaucheria* which has no mucilage/sheath and was in direct contact with flowing water (Figs. 48, 49, 50). The encrustation process appeared to be initiated by the formation of calcite crystal seeds on the surface of the empty *Vaucheria* filaments (Fig. 47). None of the *Vaucheria* samples from St. Dunstan's Well exhibited signs of calcite encrustation. Further examination revealed that many partially encrusted *Vaucheria* filaments from Whitehole

Farm Spring were reproducing asexually and sexually (Fig. 50). This enabled identification of three species as *V. sessilis* (Vaucher) de Candolle, *V. longata* Blum and *V. geminata* (Vaucher) de Candolle (John *et al.*, 2002). All live samples of *Vaucheria* from St. Dunstan's Well appeared to be in a vegetative condition and therefore unidentifiable. *Vaucheria* oospores were found in the sediment during the examination of the encrusted filaments from Whitehole Farm Spring. None of the oospores examined had any calcite crystals formed on them.







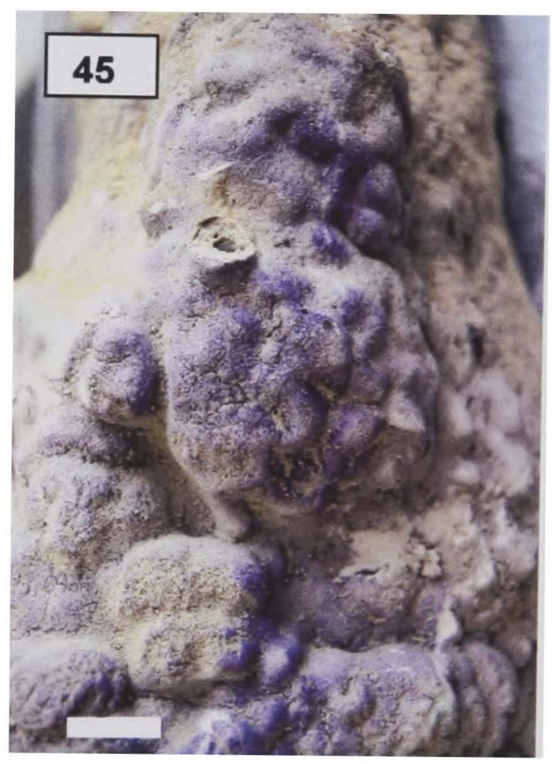


Fig. 40. Smooth surface of lithified stream crust (bar=10mm). **Fig. 41**. Lithified, dense composite tufa with evidence of several organic nuclei (bar=10mm). **Fig. 42**. Transverse section of detrital tufa showing concentric laminations around an organic nucleus (bar=40mm). **Fig. 43**. Lithified tufa crust displaying undulatory laminae (bar=10mm). **Fig. 44**. Tufa oncoid with inorganic nucleus (bar=10mm). **Fig. 45**. Surface of tufa deposited on a large branch displaying pigmentation of cyanobacterial colonies (bar=50mm).

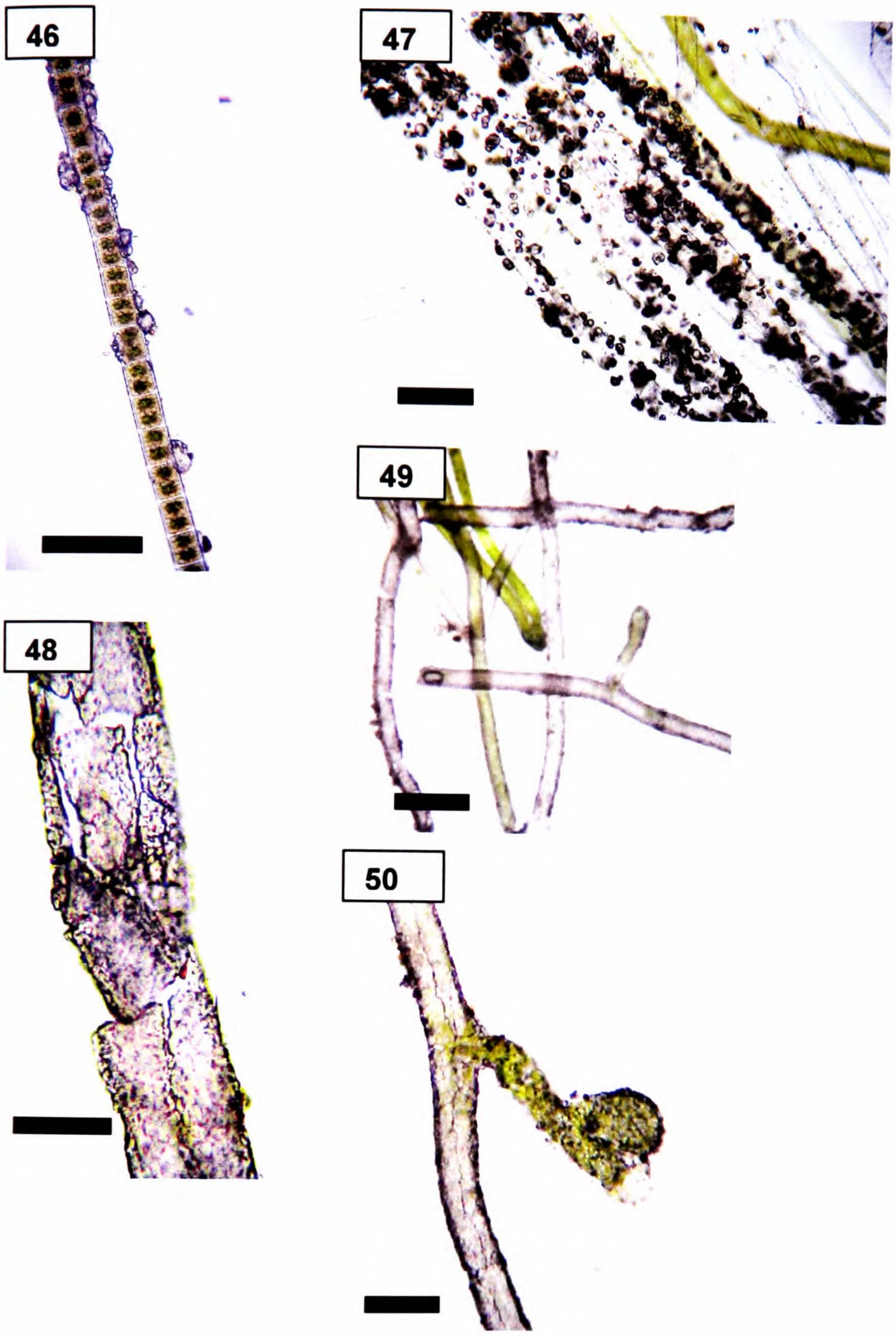


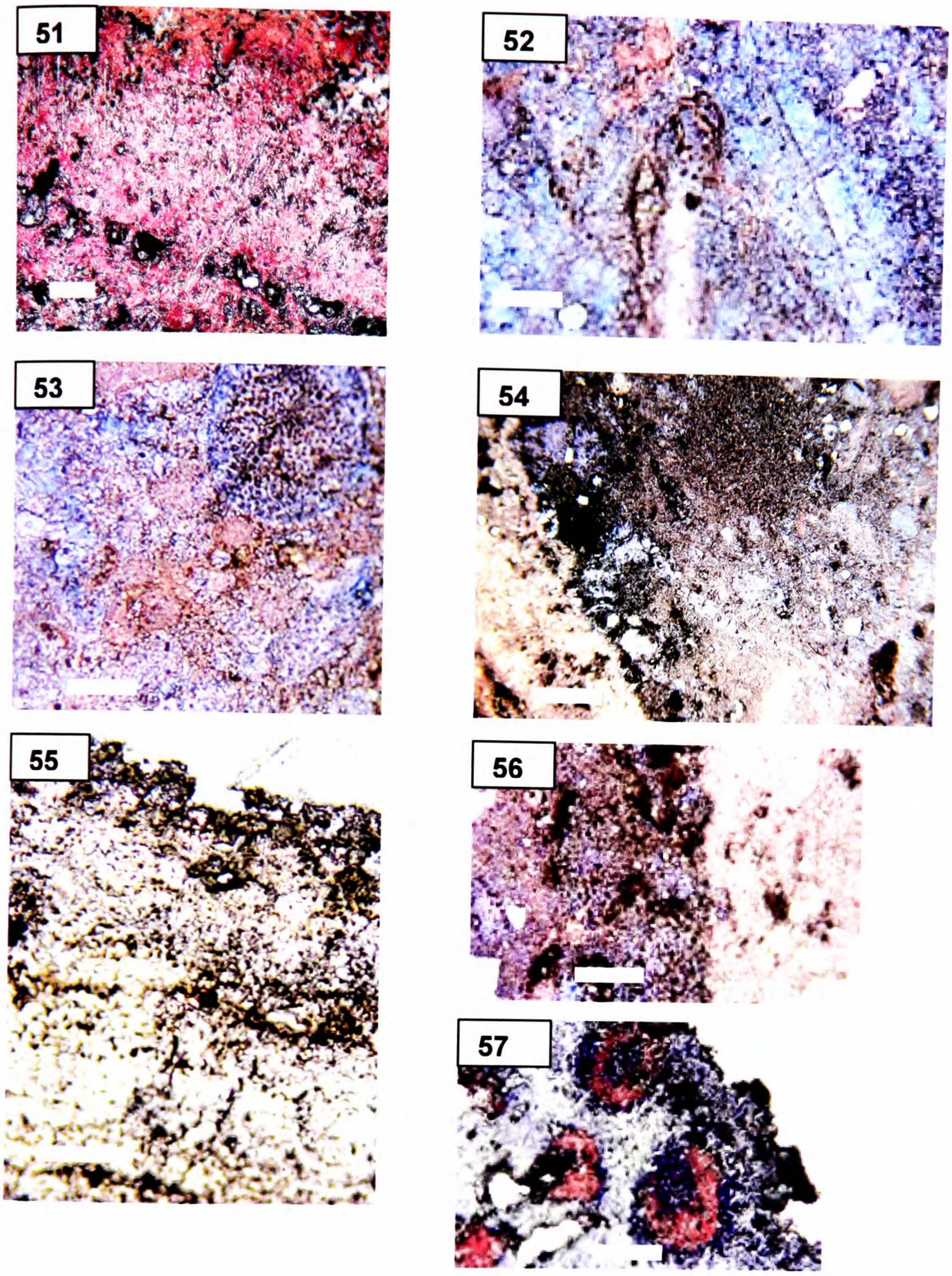
Fig. 46. A filament of *Zygnema stellinum* with calcite crystals on the outer sheath (bar=100µm). **Fig. 47**. Calcite seed crystals formed on empty *Vaucheria* filaments (bar=100µm). **Fig. 48**. Empty *Vaucheria* filament covered with plate-like calcite crystals (bar=50µm). **Fig. 49.** *Vaucheria* filaments becoming encrusted with tufa (bar=200µm). **Fig. 50**. Sexual reproduction of tufa encrusted filament of *Vaucheria longata* (bar=150µm).

4.10.4 Petrography - Stained acetate peels and microtome sections

Examination of the stained acetate peels and sections revealed a number of mineral and biological features. Mineralogically, most of the tufa samples except the composite sample in Fig. 41 which contained some ferroan dolomite, were composed of low-magnesian calcite in the form of micrite or sparite. Micrite crystals are small, < 5 µm (Adams & Mackenzie, 2001) and therefore have a larger surface area with more crystal boundaries for the absorption of stain. This is shown by the variation in intensity of the red stain as seen in Fig. 51. Ferroan calcite is shown by the presence of blue to purple colouration e.g. Figs. 52, 53. The only other element which appeared to be present in the tufa was iron, possibly in the mineral form of siderite or haematite, and shown as thin layers of brown-black stain (Fig. 55). Traces of ferrous iron and ferroan calcite were revealed in stained samples of detrital tufa, stream crusts and oncoids but not in the newly accreted tufa, moss tufa or *Vaucheria* tufa. The nuclei of the oncoid samples were composed mainly of ferroan calcite cement with some sparite and occasional quartz. The nuclei displayed compaction and reduced porosity (Fig. 54), but the tufa surrounding the nuclei was open and porous.

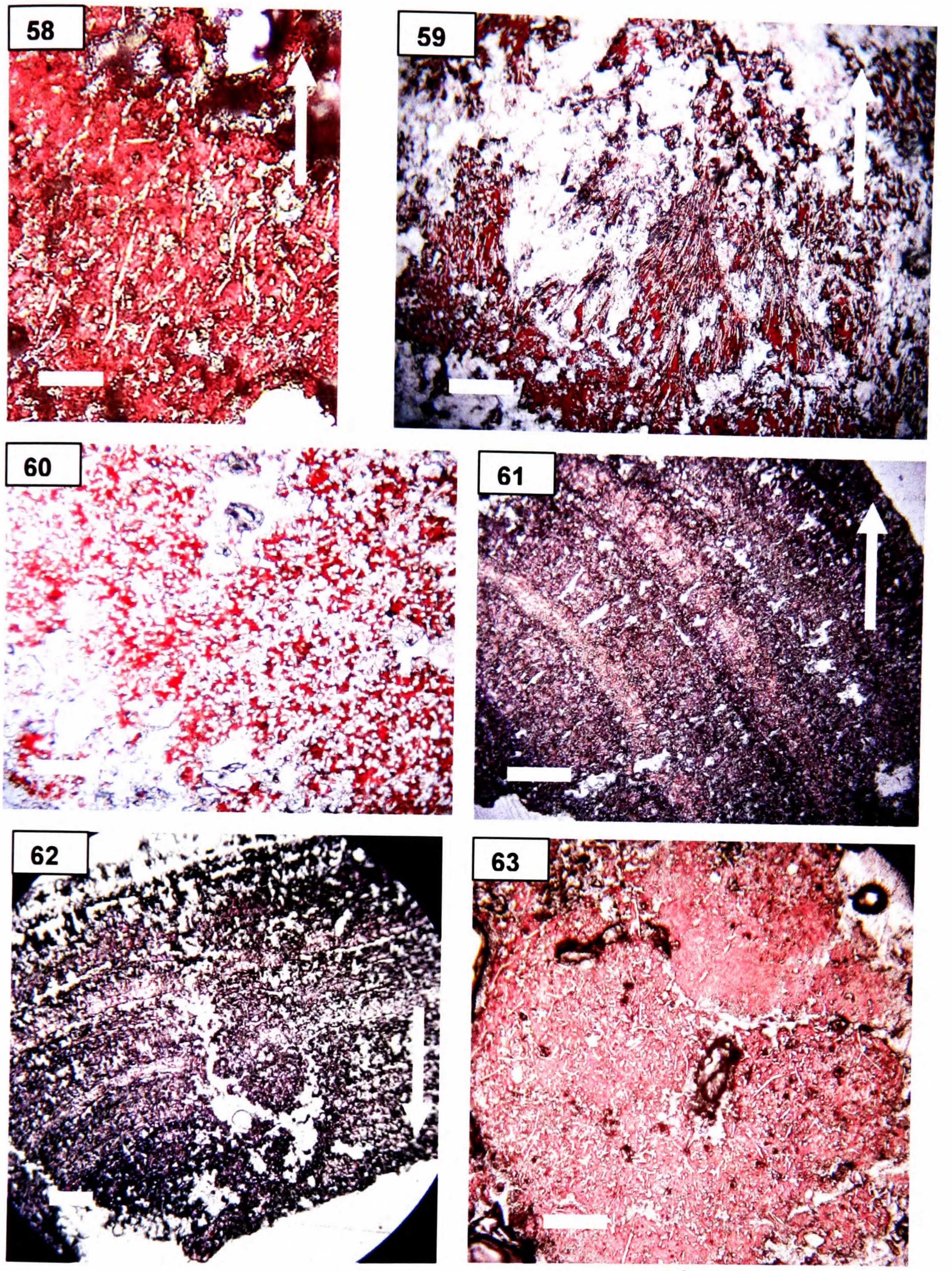
In many of the tufa samples, pores formed by the empty filament moulds remained and were observed within the red stained areas of surrounding micrite crystals (e.g. Figs. 51, 58, 59) In some lateral sections of tufa the filaments appeared to be migrating towards or boring into the surface of the deposit (Fig. 59). In a transverse section of the *Vaucheria* tufa (Fig. 60), algal filament moulds gave a perforated appearance to the surface. The filament moulds in the tufa accretion test samples ranged in external diameter from 5 µm to 10 µm with lengths from 15 µm to 50 µm. The number and mass of filament moulds decreased towards the base of the sample.

The samples of newly accreted tufa had developed, over a period of eight months (October to June), a series of alternate light and dark red stained laminae approximately 3 mm thick which were parallel to the substrate (Fig. 61). The porosity could be described as fenestral (Choquette & Pray, 1970), i.e. pore spaces larger than normal grain-supported spaces. As with previous fresh samples, the accretion test surfaces revealed an uncalcified organic layer over a substrate of calcite when stained with Methylene Blue and Alizarin Red S. Due to the small size of the lateral section of the sample (approximately 3 mm) and the thickness of the slide, it was not possible to identify the organic matter under the compound microscope. However, when viewed under the stereo microscope, calcified and uncalcified algal filaments were visible on both upper and lower surfaces (Fig. 38). The unstained upper surface showed encrusted algal filaments and calcite crystals which had formed small, hemispherical nodules less than 1 mm in diameter. A stained peel of the upper surface of Fig. 38, in transverse section, revealed a network of filament moulds in a micritic matrix within the surface of the nodules (Fig. 63).



Stained acetate peels - Minerals

Fig. 51. Transverse stained section of Fig. 60 showing calcite as sparite (pink) inner layer and micrite (red) surface layer with fenestral laminoid pores (bar=100µm). **Fig. 52.** Ferroan dolomite and calcite with some quartz in nucleus of Fig. 62 (bar=100µm). **Fig. 53.** Nuclei of oncoids in Fig. 54 showing ferroan calcite (purple/blue) and remains of organic inclusions (bar=200µm). **Fig. 54.** Sparite and ferroan calcite in composite tufa sample Fig. 59 (bar=200µm). **Fig. 55.** Layers of ferrous iron in surface of Fig. 60(bar=200µm). **Fig. 56.** Well defined junction ferroan calcite and sparite in porous nucleus of Fig 61 (bar=200µm). **Fig. 57.** Stained section from the surface of Fig. 63 showing organic matter (blue) and micrite (red) (bar=200µm) .



Stained acetate peels – Algae and cyanobacteria

(Arrow indicates upper surface orientation of sample where appropriate)

Fig. 58. Algal filament moulds surrounded by micrite in lateral section of Fig. 60 (bar=25μm). **Fig. 59.** Swarms of filament moulds in lateral section of newly accreted *Vaucheria* tufa sample (bar=100μm). **Fig. 60.** Transverse section of *Vaucheria* tufa showing alignment of filaments encrusted by micritic tufa (bar=100μm). **Fig. 61.** Tufa accretion test sample showing laminations of light and dark stained calcite with fenestral porosity (bar=150μm). **Fig. 62.** Pore space formed by decomposition of moss roots in under surface of tufa accretion test sample (bar=50μm). **Fig. 63.** Transverse section of nodular surface of Fig. 55 (bar=150μm).

4.11 DISCUSSION

The results show that there is a visible difference in biodiversity between the two study springs which is influenced by the immediate stream environment and hydrology. The conditions created by the woodland canopy at Whitehole Farm Spring encourage the growth of cyanobacteria, algae, mosses and bryophytes within the stream as these species generally prefer low light intensities (Merz, 1992). The supply of organic debris from the canopy such as leaves, seeds and woody material help the formation of distinctive and individual deposits (Pentecost *et al.*, 2000). The natural topography and gradient of the stream bed creates variations of turbulent and laminar flow conditions which encourage a diversity and abundance of plant growth.

At St. Dunstan's Well, the spring resurgence and sparsely wooded stream are more exposed to high light levels and, as a result of modification to the channel downstream, the hydroenvironmental conditions do not encourage the growth of species which are associated with the tufa deposits at Whitehole Farm and other recorded sites (Pentecost 1981,1990a; Pentecost *et al.* 2000). The combination of high discharge and the modified stream channel at St Dunstan's Well prevents the accumulation of any organic debris on the stream bed. The silty stream bed does not create a stable substrate for development of microbial biofilms (Costerton *et al.*, 1995) or primary producers such as plants and algae which play a crucial role in the formation and morphology of the varied tufa deposits at Whitehole Farm Spring.

Calcite crystallography is associated with individual species in specific environmental and hydrological conditions. For example, Pedley (1990) suggested that the speed of water flow determined the calcite crystal shape. Two macroalgal genera at Whitehole Farm Spring, namely *Zygnema* and *Vaucheria* were found to be growing under different hydrological conditions, laminar pools and flowing stream respectively. These conditions affected the morphology of calcite crystals which were forming on the algal species (Figs. 46, 48). These results compared closely with those reported by Freytet & Plet (1996) and Freytet & Verrechia (1998) who found primary crystals in the form of sparite platelets and isolated rhombohedra, respectively, associated with these two individual species.

Cyanobacteria were associated with micrite-coated sheaths and filament tubes. Upward movement towards the surface would be required to prevent motile cyanobacteria from becoming completely encrusted and to remain photosynthetic (Golubić, 1973). As the process of calcification or encrustation takes place, the organism would excrete more mucilage for gliding and protection. This would increase the possibility of further calcite nucleation. The protective properties of the mucilage can influence calcite crystal shape and the shape of the crystal is affected by the rate of crystallisation (Merz, 1992).

The iron revealed by staining (Fig. 55) could have been deposited in the sheaths of iron bacteria following the decomposition of organic matter or contained as a protective pigment in the bacterial mucilage. Bacterial and algal mucilage would appear to play a vital part in the formation of the tufa (Pentecost & Riding, 1986; Merz-Preiß & Riding, 1999). Physiological stress as a result of hydrological fluctuations or high Ca^{2+} concentrations could periodically increase the production of mucilage in motile species of cyanobacteria which colonise the deposits and plants (Emeis *et al.*, 1987). This could enhance $CaCO_3$ nucleation within or on the mucilage and/or sheath. Fluctuations in discharge would create periods of emergence and submergence for organisms at the surface of the tufa.

The newly accreted laminar tufa samples show evidence of environmental fluctuations (Fig. 61). As the tufa had accreted to a thickness of 2 –6 mm over a period of only eight months, this might suggest that development of the laminations was unlikely to have been caused by seasonal changes. They could, instead, reflect weather-related changes in hydrological conditions in the stream, or concentrations of organic matter and/or clay sediment deposited on the surfaces of the accreting tufa. Low rainfall periods can cause some areas of the lower stream channel to be virtually dry for many weeks. If the stream is dry in autumn, leaf litter and debris build up on the stream bed and are slow to decompose (pers. obs.).

It has been reported by Pentecost (2003) that calcite is deposited as micrite on the mucilaginous sheaths of the cyanobacterium *Phormidium incrustatum*. This species was present throughout the tufa-depositing stretch of the stream at Whitehole Farm Spring but not found at St. Dunstan's Well. This important species, which is common in alkaline waters, has been lost from many sites as a result of channel modification and water pollution and in areas where shading from the woodland canopy had decreased (Pentecost, 2003). It must be considered, therefore, that the modified environmental and hydrological conditions at St. Dunstan's Well are not favourable to the growth of these organisms which, under suitable conditions, could encourage the deposition of tufa within the stream.

This chapter has shown that the natural environment and biota of the stream is a major factor in the deposition and accumulation of tufa at Whitehole Farm Spring. Using the distinction by Lowenstam (1986), tufa deposition at Whitehole Farm Spring could be said to be 'biologically induced'. Biological mediation affects the rate of growth and morphology of inorganic calcite by continually increasing and modifying the surface area available for precipitation. The organisms in the tufa-depositing spring ecosystem have a clear influence on the mass, morphology, composition and fabric of the deposits and, as such, conservation of their environment is an essential part of maintaining the tufa-depositing spring system.

CHAPTER 5

CONCLUSIONS

The main results of the study, in the context of the Whitehole Farm tufa-depositing system, can now be summarised:

- The geological setting and land use of the spring catchment influence the hydrogeochemical composition of the springwater. The height of the local water table affects the volume and velocity of water travel time underground and this, in turn, is related to climate and weather conditions.
- The carbonate hydrogeochemistry of the spring determines the probability of tufa deposition. Tufa deposition at Whitehole Farm Spring is fundamentally inorganic. When the spring water is supersaturated with respect to $CaCO_3$, tufa will spontaneously precipitate and accrete on a compatible organic or inorganic substrate.
- The growth of existing calcite crystals takes priority over the formation of new nuclei (Henisch, 1970). For example, tufa is deposited on pre-existing compatible spelaeothem flowstone in the caves at St. Dunstan's Well and thus depletes the Ca^{2+} level of the water emerging at the rising in the same way that Ca^{2+} levels are depleted downstream at Whitehole Farm Spring.
- The woodland setting enhances the growth of plants such as bryophytes within the stream. The plants can act as a framework for tufa deposition and accumulation.

- Biological factors, such as bacterial and algal mucilage and sheaths can be the catalyst for tufa deposition when the water is not supersaturated. Biofilms create a site for the nucleation and growth of crystals and allow the diffusion of solutes, water and gases i.e. Ca, H_2O and CO_2. The spring provides the habitat for the organisms that influence the growth, morphology, petrology and mineralogy of the tufa deposits.
- The hydrology influences the nature and stability of the stream substrate.
- The settling tank at the Whitehole Farm Spring resurgence does not have a detrimental effect on the deposition of tufa as it buffers the stream channel against erosive storm events and also removes clay and silt from the water before it enters the stream.
- The riparian environment of the spring influences the community structure of the organisms within the spring ecosystem by affecting the input of organic debris.
- Organic debris acts as an energy source and substrate for the tufa-depositing spring ecosystem.

The work carried out in this study has achieved the main aim which was to determine whether, in the event of quarrying impacts on spring water flow, it would be possible to augment the water supply to Whitehole Farm Spring. The hydrogeological investigation has confirmed the positive hydraulic link between the new sinkhole at Pitten St and rising at Whitehole Farm Spring which could be used as a conduit for an external water supply. Base flow at the spring is provided by surface water from overflow springs in the upper Old Red Sandstone catchment. The velocity of subterranean flow from the sinkhole during a storm demonstrates the shallow nature of the limestone aquifer in the Whitehole Farm Spring catchment. The results of the hydrogeochemical investigation have shown that, although the two springs are in close proximity to each other, there are significant differences between their water chemistries. These differences suggest that , as the Carboniferous Limestone aquifer is shallow with fast flow-through times to both springs, flow from the upper geological catchments has a greater influence on the chemical characteristics of the resurging spring water than would have previously been expected. The levels of the measured parameters give an indication of the water chemistry required for tufa deposition in conjunction with the optimum environmental conditions as seen at Whitehole Farm Spring.

As a result of analysis and observation, a number of differences between the two karst springs have been revealed and are summarised in Table 12. The differences illustrate the way in which each of the components are linked together to enable Whitehole Farm Spring, its natural stream channel and woodland environment to work as a complete functioning and productive tufa-depositing ecosystem. A change in any of these components which would allow them to resemble those at St. Dunstan's Well could have a detrimental effect on the overall deposition of tufa. Processes and conditions at St. Dunstan's Well resurgence appear to work independently from those downstream. This is almost certainly due to the effects of man-made changes to the natural stream channel and bankside vegetation.

Table 12. Summary of the major differences between the two springs.

Factor	Whitehole Farm Spring	St. Dunstan's Well
Karst	Immature	Mature
Cave system	None	Well-developed
Ca levels	High	Low
NO_3 levels	Moderate	Low
Rising	Settling tank	Natural rising
Stream sediment	Low	Periodically high
Stream channel	Natural	Modified
Stream bed	Rocky	Silty
Stream substrate	Stable	Unstable
Flow volume	Low	High
Banksides	Mature woodland	Sparse woodland
Light levels	Low	High
Organic matter	High	Low
Biodiversity	High	Low
Tufa	Present	Not present

Goudie *et al.* (1993) and Griffiths & Pedley (1995) suggested that there had been a decline in tufa deposition in the UK and Europe since the mid-

Holocene. Several climatic and anthropogenic hypotheses were postulated to explain the decline although Baker & Simms (1998) argued that the tufa decline was only applicable to large-scale deposits (> 1000 m^2) and not small sites (< 1000 m^2). However, Goudie *et al.* (1993) considered the effects of changes in catchment conditions on the ecology of the microorganisms which, in this study, have been shown to play a considerable role in the deposition and formation of the tufa deposits. It can be seen from the previous summarised points that tufa deposition at Whitehole Farm Spring, although predominantly controlled by inorganic processes, is also biologically and environmentally influenced. Therefore these factors must be considered in addition to hydrogeochemistry in the maintenance and conservation of the deposits. In the case of Whitehole Farm Spring, this study has shown that it would be possible to augment the water supply in the event of discharge diminution but in order to maintain the varied geomorphological structure of the site, the range of lotic and riparian habitats within and around the spring and its stream must be protected. Riparian vegetation, particularly as leaf litter, supplies the organic matter required as a primary energy source for springs where often, autochthonous production is naturally low (Rosi-Marshall & Wallace, 2002). The organic surfaces are rapidly colonised by microorganisms such as bacteria, fungi and protozoans (Cummins, 1974). This action increases the surface area available for tufa accretion and subsequent further colonisation by microorganisms. In this way, the stream biota enhance tufa deposition. The riparian canopy also provides the cool, shaded conditions required for the optimum growth of cyanobacteria, algal and bryophyte species within the stream. These processes enable the tufa ecosystem to become self-sustaining.

This study has examined some of the components of the karst spring system and has underlined the complex and necessary interactions between abiotic and biotic processes taking place within a tufa-depositing water body. In the long-term, however, further work on karst system processes at catchment-scale is recommended in order to develop an effective regime for the monitoring and conservation of tufa-depositing springs. By using a multidisciplinary approach, it has also been revealed that biological and environmental factors within the spring catchment influence the deposition, composition and morphology of the tufa deposits. This study has provided a detailed contribution to knowledge of the hydrogeology, hydrogeochemistry and ecology of karst springs in the Mells Valley and the data on the two springs have provided a baseline for the future assessment of tufa deposition in karst springs in other Carboniferous Limestone catchments. The study has also highlighted the need for the conservation of not only the tufa deposits, but also the protection of the natural environment of the stream and its biota.

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