Proc. Univ. Bristol Spelaeol. Soc., 2001, 22 (2), 157-181

HYDROCHEMISTRY OF STREAMS WHICH ENTER ST. CUTHBERT'S SWALLET, PRIDDY, SOMERSET.

by

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ABSTRACT

The current surface hydrology associated with St. Cuthbert's Swallet was studied between 1994 and 1997 by frequently sampling at 3 sites. The study period included spells of heavy rainfall in November 1994 and spring 1995 and a drought of historic proportions in 1995 when the Mineries Pool Outflow stream (the largest stream entering the cave) and a nearby spring stopped flowing. When flow of the Pool Outflow stream resumed, a huge surge of calcium sulphate appeared in its water. Most hydrochemical properties showed very low variability at Fair Lady Well. Periods of intensive sampling enabled the response of hydrochemical features to stream size to be investigated. Total, calcium and alkaline hardness varied inversely with stream size at the Pool outflow stream and at the main stream sink. Aggressiveness varied with stream size only at the Main Stream Sink. The mean concentration of nitrate in St. Cuthbert's Stream was below 4×10^{-5} M. Concentrations of potassium and nitrate showed seasonal variations except at Fair Lady Well. After the 1995 drought, the long delay before the Fair Lady Well flow restarted implies that the aquifer has an unknown lower point of discharge which had continued to flow after the well stopped flowing.

INTRODUCTION

The physical and chemical characteristics of a stream entering a cave system are important to considerations of how the stream will interact with the cave. Things that depend crucially on the stream's hydrochemical characteristics, include:

1. How, where and how much limestone solution will take place;
2. Whether the stream will deposit dripstone formations and
3. How the physical and chemical characteristics of the stream will change as the

These factors are important in determining where changes are currently taking place in cave systems and inferred past characteristics may help in explaining how various features developed. Such considerations are important in helping to explain some of the differences between nearby cave systems, such as Swildon's Hole, Eastwater Cavern, and St. Cuthbert's Swallet.

Stenner studied aspects of the hydrology of St. Cuthbert's Swallet between 1965 and 1973 and published preliminary reports (Stenner, 1968, 1977). Sets of samples had been collected in normal, high and low water conditions, in summer and in winter. The hydrology of the streams which enter St. Cuthbert's Swallet has been described previously (Stenner, 1968, Atkinson, 1971, Irwin, 1991). However, in 1991, a major change was noticed. The Mineries Pool Outflow Stream, formerly known as Plantation Stream, had changed its course (Stenner, 1997). Stream distribution changes and changes in the characteristics of the streams in the New and Old Routes in the cave and around Plantation Junction, were clearly very large. To produce an account of the current hydrology of the cave, much of the work would need to be repeated.

The general outline of the studies

Studies of the present hydrochemical characteristics of the streams started in May 1994. The aim was to describe the current surface hydrology, and quantify the changes. Three stream sites on the surface were chosen for intensive study (see Figure 1). They were the Outflow Stream of the Mineries Pool, St. Cuthbert's Main Stream close to the Main Stream Sink and (after a short delay) the Fair Lady Well at the spring close to the Mineries Pool. The three sites were studied for a period of more than three years, and irregular comprehensive collections of water samples, temperatures and stream size data from the cave streams were made by E. Sandford and J. Williams.

A description of the changes in stream distribution in the cave has been published (Stenner, 1997). The unprecedented calcium sulphate surge in the Mineries Pool Outflow stream that followed the summer drought in 1995 has also been described (Heathwaite, *et al*, 1999).

Changes in the water during its passage from surface sinks to the open cave were measured, and compared with similar changes in the streams before Plantation Stream changed its course. These topics have been described and discussed separately (Knights, *et al*, 2001).

The present paper is concerned with data from the three surface stream sites. The present hydro-chemical characteristics of the streams at the three sites are described and compared with the previous characteristics at the same sites. Differences in patterns of variability are noted, and links between various characteristics are described.

The reason for including Ladywell Stream in the study

Although water leaking from the stream had been traced to an inlet in the cave in 1972, to the Coral Series stream, the main flow of the stream has never been traced. It is suspected that it eventually flows to Wookey Hole. In November 1994, water was overflowing from the stream into a marsh that had previously been a source of a hidden tributary of Plantation Stream. This tributary (shown in Stenner, 1997; Figure 1) is an important contributor to the Plantation Stream inlet in the cave, and for this reason, the Ladywell Stream was included in the study from that time on.

Special features of the study sites

Streams entering St. Cuthbert's Swallet flow through areas of marsh (Heathwaite, *et al*, 1999), which buffer the response of the streams to rainfall (Irwin, 1991). No water is pumped from the aquifers that supply these streams, and the streams are the largest streams on Central Mendip not affected by abstraction. They continue to flow in times of drought long after most other surface streams on the Mendip plateau have dried up (Atkinson, 1971). Fair Lady Well is so reliable that until about 1950 it was the source of potable water for part of the village of Priddy.

Since the St. Cuthbert's Leadworks stopped production in 1908, the valley floor has been derelict, except for the valley floor upstream of the Mineries Pool dam to and including Waldegrave Pool, which is a nature reserve now managed by the Somerset Wildlife Trust. The land use of the catchment area surrounding the valley floor is limited to grazing cattle on the summit of North Hill, and forestry, largely conifer plantation, on Stockhill. The usage has been unchanged for many years, except for the cropping of part of Stockhill forestry in 1996.

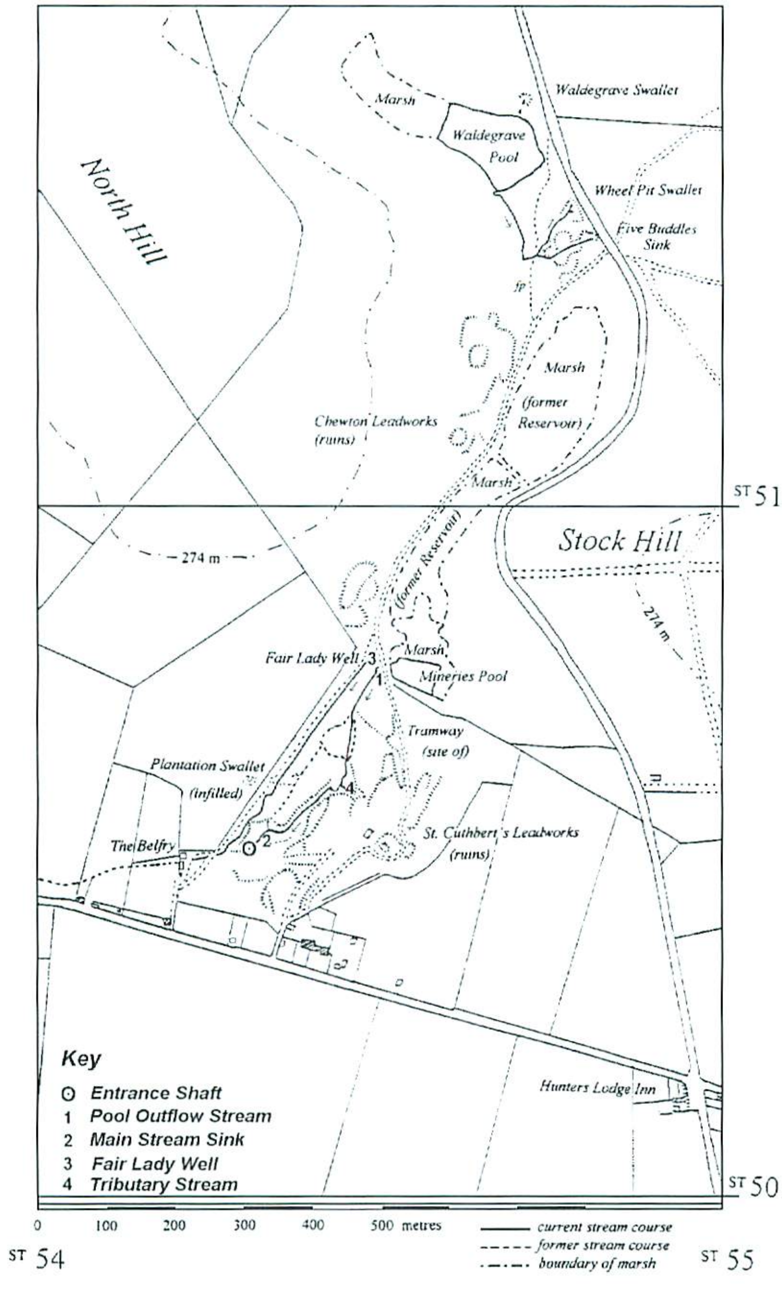

Figure 1. *Area map: Streams draining to St. Cuthbert's Swallet Somerset*
Reproduced from the Ordnance Survey map with the permission of Her Majesty's Stationery Office,

Additional detail from Stenner and Stenner, 1998.

Flow in the newly discovered tributary complex near the Maypole Overflow Corner: a chronological summary

This section is a record of the activity in the area immediately upstream of the Maypole Overflow Corner. Irregular substantial leaks in the Ladywell Stream had played a large part in this activity. Flow from the marsh continued at least two months after the leaks had been repaired.

Winter in 1994/5 was unusually wet, with particularly heavy rain in November 1994 and between January and May 1995. Water flowed in the bed of the former Plantation Stream (now normally dry), part of the water coming from an overflow from Ladywell stream.

A small network of trickles had previously been an undiscovered tributary of the former Plantation Stream, and is now the major source of water entering St. Cuthbert's Swallet as the Plantation Stream inlet (Stenner, 1997).

In November 1994, January and February 1995, flow in the newly located tributary complex overflowed the old stream course at the Maypole Overflow corner, sinking in the Maypole Sink and mixing with water from St. Cuthbert's stream.

After heavy rain in the winters of 1995/6, 1996/7 and 1997/8, no surface stream was seen in the bed of the former Plantation Stream at the Maypole Overflow Corner, although the stream bed a few metres upstream was often very boggy. Local surface runoff probably took place at the peaks of heavy rainstorms.

After the unusually wet spring of 1995 came a drought of historic magnitude (widely reported in the press to be the most severe since the seventeenth century). The Pool Outflow

There was another unusually severe drought in the summer of 1996, and an extremely unusual dry midwinter spell from mid-December 1996 until February 1997.

After heavy rainfall in December 1998, there was a good flow of water into the Maypole Overflow Corner, with overflow into the Maypole Sink on 3/01/99.

Ladywell Stream was choked with dead leaves and vegetation, and overflowing into marsh at two points close to one another. The blockage was cleared, but overflow at both points continued on 10/01/99 and 17/01/99 and overflow from Maypole Overflow Corner into Maypole Sink continued. By 24/01/99, one of the Ladywell Stream leaks had been sealed, but a trickle was still leaking away from the second. Water was still flowing into Maypole Overflow Corner, but water was static in the overflow channel to the Maypole sink. The position was the same on 31/01/99.

On 7/02/99 and 21/02/99, there were no leaks from Ladywell Stream, and only a small trickle into Maypole Overflow Corner, and no overflow.

On 18/04/99 and 25/04/99, although no water reached Maypole Overflow Corner, there was flowing water in the old Plantation Stream bed 10 m upstream, and a good flow of water out of a nearby marsh flowing towards the former bed of the Plantation stream but not reaching it.

After more heavy rain, a trickle into Maypole Overflow Corner resumed on 2/05/99, with no overflow. There was no leakage from Ladywell Stream.

By 9/05/99 flow into Maypole Overflow Corner had ceased, but there was flow in the old streambed

On 16/05/99 and 30/05/99 there was still flow in the old streambed 10 m upstream, and visible flow from the marsh. By 14/07/99 the entire former Plantation Stream system was dry.

The observations have been described in detail, since they demonstrate several facts:
1. While at times overflow from Ladywell Stream contributes to the flow in the hidden

2. A large proportion of the water which reaches Maypole Overflow Corner sinks at this site in low and moderate flow, and only in high flow does it overflow to the Maypole Sink.
3. A considerable proportion of the flow in the hidden tributary sinks before it reaches the Maypole Overflow Corner.

The hidden tributary stream is important when considering changes which were observed in the former Plantation Stream between the Mineries Pool and Plantation Swallet between 1966 and 1973, discussed elsewhere (Knights, *et al.* 2001) and is a major source of the present inlet stream at Plantation Junction.

In a recent paper (Stenner, 1997) it was reported that since 1970 the Ladywell Stream had no longer appeared on the far side of the Belfry. A good flow has since reappeared and was first seen by Stenner on 3/01/99. Apart from a very short time in the summer of 1999, when the flow of Ladywell Stream was too low to overflow from the Drinking Pond at the Belfry, the stream has continued to emerge the far side of the Belfry (to the time of writing in January 2001).

EXPERIMENTAL PROCEDURES

Water samples were collected from three sites; the Mineries Pool Outflow Stream, the Main Stream Sink of St. Cuthbert's Stream and Fair Lady Well. The location of the sites is shown in Figure 1. Duplicate samples for aggressiveness determinations were saturated with AnalaR $CaCO_3$ at the site. Whenever sediment was visible in the stream, the sample was filtered through an 11 cm diameter Whatman 541 paper at the time of collection. Samples were kept cool and in the dark until analysed.

Water temperatures were measured for most of the study period, using either a calibrated electronic or a mercury-in-glass thermometer, both of which were graduated to 0.1 °C. The stream size (Q, in litres/minute) of the Pool Outflow stream and St. Cuthbert's Stream, close to the Main Stream Sink, were measured by salt dilution, using a simple constant flow apparatus and standard KCl solutions (Stenner and Stenner, *in prep*). A standard KCl solution was added from a constant head bottle, and water samples were collected from a suitable downstream site until potassium in the samples reached a stable plateau. From the data the stream size was calculated by a standard Physics procedure, called the Method of Mixtures. In many of the regressions involving stream size (Q) that were investigated, a Discharge Function ($Q^{-0.4}$) was used. This power function is related to the time taken for a stream to flow between two given points, and using this function has been shown to be more likely to yield a significant correlation than other functions (such as square root, or inverse) with related factors.

Various leakages from Ladywell stream into the cave, via storage in marshes, have taken place at irregular intervals. Stream size values of this stream, which would not have contributed directly to an understanding of the hydrology of the cave, were not measured.

To calculate ion balances, and give a check on the reliability of the laboratory work, it was necessary to analyse samples for all ions present in significant concentrations; total hardness, sodium, potassium, bicarbonate, chloride, sulphate and nitrate. Aggressiveness to calcium carbonate was measured, and the results were scrutinised for unusual results that would require the inclusion of concentrations of additional ions from the calcium carbonate/water/carbon dioxide system in the ion balance calculations. Magnesium was determined to enable total hardness data to be divided into calcium and magnesium. Because pH can be reliably calculated from hardness and aggressiveness data, pH was not included in the list of measurements.

Anion analyses: Nitrate and sulphate species were determined using a Dionex Model 2020i ion chromatograph. Chloride concentrations were determined by titration with standard 0.02M silver nitrate (using 25 ml aliquots, and potassium chromate indicator). Bicarbonates were determined (as alkaline hardness) by titrating 25 ml aliquots with standard 0.02 M HCl. Ion Chromatography (IC) indicated that no other ions (notably fluoride, phosphate, bromide or iodide) were present in detectable concentrations.

Cation analyses: Total hardness and aggressiveness to $CaCO_3$ were determined by titrating 25 ml aliquots with EDTA (standardised with magnesium iodate) and magnesium was determined by atomic absorption spectrophotometry (AAS). Flame emission spectrophotometry (FES) was used to determine sodium and potassium concentrations.

Fuller details of the methods used to determine the concentrations of all anions and cations necessary to calculate ion balances have been published elsewhere (Knights and Stenner, 1999), together with an examination of the experimental precision. All concentrations were expressed as $10^5 \times$ Molarity, the unit most appropriate for the investigation of ion balances.

Analyses for total and alkaline hardness and aggressiveness were carried out as soon as possible, usually within 6 hours, and always within 24 hours, except for alkaline hardness in the first 5 months of the study. In these exceptions there were delays of up to a week before potentiometric titrations could be used and many of the results were shown to be seriously inaccurate and deleted from the databases. From January 1995 onwards, the endpoint of alkaline hardness titrations was found colorimetrically, using BDH 4.5 indicator, as soon as possible after collection, ending the delays in alkaline hardness determinations and consequent errors. Except in a small number of cases, total hardness titrations were carried out in duplicate. In all other analyses, small numbers of determinations were made in replicate, from single rather than replicate samples, to provide estimates of standard errors. Apart from total hardness and alkalinity, the other ions which are known to be stable in suitably stored samples were analysed as soon as was convenient.

For the first eighteen months the sites were sampled at approximately four weekly intervals, but for the final period of study the frequency of sampling was varied. The intent was to determine firstly changes of hydrochemical characteristics during periods with no rain, in summer and in winter, and secondly changes which followed rainstorms.

ACCURACY AND PRECISION

The following standard errors were calculated (as $10^5 \times$ Molar, ~ ppm as $CaCO_3$):

Total hardness, calcium and aggressiveness to $CaCO_3$, all 0.8; alkaline hardness 3.0; Non-alkaline hardness, 3.8; magnesium, 0.17; sodium, 0.13; potassium, 0.05; chloride, 2.6; sulphate, 0.3; nitrate, 0.23.

Stream size measurements failed at the Pool Outflow on 7 occasions and at the Cave Sink on 4 occasions. By referring to ratios of the sizes of the two streams and the stream size at the other site on the date in question, it was possible to make an estimate of the stream size on 7 of these 11 occasions. These estimates (marked to distinguish them from measured data) have been included in Figures 13 and 14. These estimates were not included in the database used to generate statistical summaries, or correlations with other measurements, or any other figures.

RESULTS AND DISCUSSION

Tables 1 to 3 summarise the hydrochemical characteristics of the three sites. Table 3 also shows results for the four samples taken from Fair Lady Well between 13/08/95 and 7/11/95 when the spring was not flowing. The time series graphs, Figures 2 to 14, show visually the major characteristics of each quantity. Four aspects of the data were of particular interest:

1. How the various quantities differ between the three sites,
2. The variability and the extent of the variability of each quantity, through time at each site and between sites,
3. If there is any regular trend in variability, and in particular if there is evidence for periodicity, and
4. Whether or not there is a link between variability in different quantities (for example with stream size).

Site characteristics and their inter-relationships

Figures 2 to 14 show very clearly that the characteristics of Fair Lady Well differ significantly from those of the other two sites, in spite of the proximity of the spring to Mineries Pool. Many of the properties of Fair Lady Well are much less variable than those of the other two sites. For temperature, calcium alkaline and total hardness, sulphate and potassium, the variability is outstandingly low, and it is especially noteworthy that there was no evidence whatsoever of seasonal or discharge-related variability in this spring. The hydrology of the spring must differ fundamentally from that of the other two sites.

The sulphate surge that developed after the summer drought in 1995 can be seen in Figure 4. The highest values of chloride and sodium concentrations recorded in the Pool Outflow Stream (Figures 7 and 10 respectively) coincided with the peak of the sulphate surge. Details of the normal sulphate levels, excluding data from the surge, can be seen in Figure 5.

The derived quantity non-alkaline hardness, was described by Heathwaite, *et al.* (1999). The regression equations for the non-alkaline hardness/sulphate relationships at the Pool Outflow and main stream sites yielded linear 1:1 relationships with highly significant correlation coefficients.

	Excluding calcium sulphate event						During calcium sulphate event						All data					
	Mean	No.	S.D.	R.S.D	Max	Min	Mean	No.	S.D.	R.S.D	Max	Min	Mean	No.	S.D.	R.S.D	Max	Min
Temperature	11.8	25	5.01	42.5	20.3	3.1	6.96	13	3.41	49.1	12.6	1.8	9.64	40	5.41	56.1	20.3	1.8
Discharge	484	45	759	157	4230	0	936	12	1013	108	3940	213	579	57	830	143	4230	0
Tot. hard.	93.3	47	19.8	21.2	135.8	50.8	98.3	13	24.5	24.9	135.3	60.8	94.4	60	20.8	22	135.8	50.8
Aggress.	13.1	47	5.84	44.6	28	4.3	14.5	13	6.31	43.5	25.1	6	13.4	60	5.92	44.2	28	4.3
Mg	13.8	47	3.64	26.4	21.1	8.3	14.2	13	5.66	39.9	29.4	8.7	13.8	60	4.1	29.7	29.4	8.3
Ca	79.6	47	17.1	21.5	118	42.5	84.2	13	20.6	24.5	111.2	52	80.6	60	17.8	22.1	118	42.5
Alk. hard.	81.3	41	23	28.3	124.8	32.8	62.3	13	18.1	29.1	88.4	40.1	76.7	54	23.2	30.3	124.8	32.8
Non-alk. hard.	10.7	41	5.02	46.9	20.8	2.8	36	13	19.2	53.2	85.6	19.4	16.8	54	14.8	88.3	85.6	2.8
SO_4	10.1	39	3.67	36.3	17.2	4.8	35.4	13	5.31	15	51.3	30.5	16.2	52	15.5	95.4	51.3	4.8
NO_3	3.6	39	2.85	79.4	10.7	0.2	5.6	13	3.31	59.1	10.9	1.5	4.1	52	3.06	74.6	10.7	0.2
Cl	34.7	47	3.4	9.8	42.3	26.8	35.3	13	3.78	10.7	43.4	30.3	34.9	60	3.83	11	43.4	26.8
K	2.48	47	1.34	54.2	5.8	0	3.3	13	1.21	36.6	5	1.1	2.65	60	1.35	51	5.8	0
Na	33.2	47	3.38	10.2	40.5	22.2	31.3	13	4.9	15.7	43.4	24.2	33.6	60	3.55	10.6	43.4	22.2
Ion balance													-1.18	52	6.57	-557		

Table 1. *Characteristics of the Mineries Pool Outflow Stream. Concentrations 10^5* x *Molar, (ion balance univalent) discharge l min^{-1}*

	Excluding calcium sulphate event						During calcium sulphate event						All data					
	Mean	No.	S.D.	R.S.D	Max	Min	Mean	No.	S.D.	R.S.D	Max	Min	Mean	No.	S.D.	R.S.D	Max	Min
Temperature	11.04	57	2.78	25.2	16	3.8	7.08	13	2.85	40.3	11.8	2.8	10.3	70	3.18	30.9	16	2.8
Discharge	770	79	922	120	5450	141	1023	11	464	45	1780	446	793	91	880	111	5450	141
Tot. hard.	136.9	84	27.1	19.8	185	80.7	124	13	22.9	18.5	160.4	85.5	135.2	97	26.8	19.9	185	80.7
Aggress.	-1.7	83	3.69	-217	6	-15	0.1	13	1.92	1915	5.6	-1.6	-1.48	96	3.55	-240	6	-15
Mg	16.5	84	3.29	19.9	24.3	10.2	14.4	13	3.3	22.9	21.5	9	16.2	97	3.35	20.7	24.3	9
Ca	120.5	84	24.8	20.5	168.4	70.1	109.7	13	20.2	18.5	145.8	76.5	119	97	24.4	20.5	168.4	70.1
Alk. hard.	126.6	78	27.3	21.5	171.3	67.3	95.6	13	17.5	18.3	128	66	122.2	91	28.2	23	171.3	66
Non-alk. hard.	10.6	78	2.8	26.4	17.7	5.1	28.4	13	10.6	37.4	54.6	16.4	13.2	91	7.8	59.1	54.6	5.1
SO_4	11	76	1.66	15.1	15.7	8	27.3	13	11.6	42.3	54.1	16.1	13.4	89	7.38	55.1	54.1	8
NO_3	3.63	75	2.01	55.5	9.1	0.2	5.59	13	2.4	43	10.7	2	3.93	88	2.16	55	10.7	0.2
Cl	30.3	84	3.11	10.2	39.3	18.7	31.9	13	3.89	12.2	40.1	28.1	30.5	97	3.25	10.6	40.1	18.7
K	2.88	84	1.83	63.6	15.4	0.3	3.15	13	0.89	26.1	4	1.9	2.92	97	1.73	59.2	15.4	0.3
Na	29.8	84	2.71	9.1	36.7	22.1	34.5	13	4.43	12.9	40.9	25.4	30.4	97	3.37	11.1	40.9	22.1
Ion balance													-1.52	90	5.67	-373		

Table 2. *Characteristics of St Cuthbert's Stream at the Main Cave Sink. Concentrations* 10^5 x *Molar, (ion balance univalent) discharge l* min^{-1}

	Mean	No.	S.D.	R.S.D.	Max	Min	13/08/95	24/08/95	27/09/95	18/10/95
Temperature	10	28	0.32	3.2	11.2	9.5	14	14.5	10.9	9.7
Tot. hard	160.8	46	5.1	3.1	168.5	149.1	181.4	197.1	136.8	164
Aggress.	4.9	45	2.43	49.5	11.4	0	-5.8	-3.6	15.9	0.8
Mg	25	46	3.81	15.2	35.2	18.2	21.3	24.3	14.2	23.2
Ca	135.8	46	4.65	3.4	143.9	123.7	160.1	172.8	122.6	140.8
Alk. hard.	150.9	45	5.06	3.4	159.4	139.1	171.7	194.5	88.4	150.5
Non-alk. hard.	10	45	2.73	27.3	15	4.7	9.7	2.6	48.4	13.6
SO_4	8.23	42	0.44	5.3	9.5	7.5	8.6	16.8	24.5	8.8
NO_3	11.9	42	1.5	12.6	16.6	8.6	15.2	72.8	20	11.3
Cl	27.5	44	2.25	8.6	32.1	22	38.5	72.2	74.6	29.7
K	3.77	46	0.32	8.6	4.8	3.1	6.1	35.3	3.9	3.6
Na	28.1	46	0.89	3.2	29.7	25.7	29.8	45.5	47	25.2
Ion balance	-4.3	41	6.06	-141			-16	-93	4	-3

Table 3. *Characteristics of the Fair Lady Well.. Concentrations 10^5* x *Molar, (ion balance univalent) discharge l min^{-1}*

Large variability at the Pool Outflow and Main Stream Sink sites can be seen in temperature, and in calcium alkaline and total hardness, magnesium, nitrate and potassium concentrations. However, temperature and magnesium, nitrate and potassium concentrations showed no association whatsoever with stream size. Variations in sulphate, excluding the surge, were not related with stream size in a straightforward manner. There were high levels of sulphate following the first periods of heavy rainfall after a dry spell, similar to patterns found in water draining peat bogs in West Sedgemoor (Heathwaite, *et al.* 1999). It was suggested by Heathwaite that during drought conditions, sulphur is deposited in the marshes in an intermediate form from whence it is readily flushed into the streams by the first major rainfall, an explanation that closely matches the observed time series sulphate graph.

The aggressiveness of St. Cuthbert's stream at the Main Stream Sink had a simple relationship with stream size; it was super-saturated at low stream size, and under-saturated at high stream size (Figure 15). As the total hardness at the Main Stream Sink had a high correlation with stream size, the aggressiveness at this site also had a high correlation with total hardness (Figure 16). The aggressiveness of the Pool Outflow Stream had no such simple relationships with either stream size or total hardness.

The normal interrelationship between magnesium and sulphate, which changed significantly during the calcium sulphate event, is detailed elsewhere (Heathwaite, *et al.* 1999, Figures 5 and 6).

At the Pool Outflow and the Main Stream Sink, magnesium had high correlations with three related quantities; total hardness, alkaline hardness and calcium; that with alkaline hardness is shown in Heathwaite, *et al.* 1999, Figure 10. The relationships reflect the Ca:Mg ratios in the limestones being dissolved.

The normal calcium/alkaline hardness relationships, which were distorted during the calcium sulphate event, are also shown elsewhere (Heathwaite, *et al.* 1999, Figures 7 and 8).

At the Fair Lady Well, the relationships of non-alkaline hardness with sulphate, magnesium with sulphate, magnesium with calcium and calcium with alkaline hardness were uninformative, a consequence of the very low variability of the quantities at this site (see Figures 5, 7 and 10 in Heathwaite, *et al.* 1999). Further work will be needed to find how stable this situation is.

At all three sites, examinations of interrelationships involving sodium, chloride and potassium were statistically insignificant. The fact that sodium concentrations showed the lowest variation and the lowest values in Fair Lady Well was noted, while both potassium and nitrate concentrations were least variable and highest in value at that site (Tables 1 to 3, and Figures 10, 7 and 11).

The relationship between dissolved calcium hydrogen carbonate and stream size

Figures 13 and 14 show the relationship between total hardness and discharge at the Pool Outflow and Main Stream Sink respectively. The relationships between calcium and stream size, and between alkaline hardness and stream size were so similar to Figures 13 and 14 that it was not sensible to include them in this paper. The underlying inverse relationship between dissolved calcium hydrogen carbonate and stream size is very clear. While the phenomenon is well known in similar studies in other Karst areas, such as that described by Bray, 1997, its reason is not certain. It is possible that the factor limiting limestone solution at any site is the available concentration of carbon dioxide. At higher than normal stream size, the available carbon dioxide will dissolve less calcite.

At the Main Stream Sink and at the Pool Outflow, the correlation between alkaline hardness and stream size was high (see Heathwaite, *et al.* 1999, p259 and p261 Figure 9). The relationship between dissolved calcium, hydrogen, calcite and stream size calls for detailed comments, because there were occasions when details in the data did not fit the usual pattern. In Figure 14, significant fluctuations in total hardness can be seen at the Main Stream sink between 20/11/95 and 24/03/96. Although the changes in hardness between successive troughs and peaks were similar in magnitude, they were clearly not caused by changes in stream size which were similar in magnitude. Very large changes in stream size could result in relatively small changes in hardness, as between 13/02/96 and 27/02/96, while, conversely, modest changes in stream size could result in large changes in hardness, as between 30/11/95 and 15/12/95. Similar discrepancies were also noticed at Ogof Ffynnon Ddu by Bray (1996). The abnormal data were examined in closer detail, because it appeared that sometimes, when the stream size had very recently risen to a high value, the hardness was higher than expected; possibly because hardness was slower than stream size to respond to the rainfall. Conversely, there were occasions when the stream size had fallen after a flood, the hardness was lower than expected, possibly because hardness was slower than stream size to recover after rainfall.

At the Main Stream Sink, where sampling was most intensive, there were instances when in base-flow conditions, hardness often fell sharply in response to modest increases of stream size. For example, between 9/08/96 and 12/08/96, the stream size of St. Cuthbert's stream at the sink rose from 192 l/min to 207 l/min, but the total hardness fell from 176 to 151 ppm as $CaCO_3$. At high stream size, conversely, very large increases in stream size sometimes caused small decreases in hardness.

The total hardness of the stream was therefore, effectively restricted to a definite band of values, within which it was related to stream size. Close to the limits of the band, at upper and lower limits, it is increasingly difficult for stream size changes to cause proportionate hardness changes. A similar result was found in Ogof Ffynnon Ddu (Bray, 1996), although the values of the upper and lower limits were obviously not the same.

Between 23/05/96 and 7/06/96, the intensity of sampling was increased to investigate detailed response of stream size and hardness to immediate rainfall. The streams were sampled immediately before forecast rainfall arrived, and again soon after rain stopped. The results, presented in Table 4, show further examples of anomalies.

Date	Stream size l/min	Total hardness, ppm $CaCO_3$
23/05/96	550	125
24/05/96	1,380	106
26/05/96	980	106
28/05/96	940	102
31/05/96	755	108
3/06/96	615	118
7/06/96	350	133

Table 4. *Stream size and total hardness of St. Cuthbert's Stream at the Main Stream Sink between 23/05/96 and 7/06/96.*

The results show that on 24/05/96 the total hardness was higher than might have been expected, while on 31/05/96 it was lower. Similar anomalous hardness results were obtained between 21/08/96 and 10/09/96. Perhaps a more detailed study of the relative rates of response of stream size and salt concentrations to rainfall, with intensive sampling at short time intervals and detailed measurement of local rainfall, would clarify such apparent anomalies.

Because in limestone waters alkaline hardness, calcium and total hardness share the same origin (limestone with a high content of calcium carbonate which has been dissolved by water containing dissolved carbon dioxide), all three share similar relationships with stream size. The correlation coefficients for the alkaline hardness/stream size regressions were higher at the Main Stream Sink and at the Pool Outflow Stream than those for total hardness/stream size and calcium/stream size. This highly unusual result is caused by the fact that the calcium sulphate surge had distorted the normal calcium/stream size and total hardness/stream size relationships (Heathwaite *et al.* 1999, p259). However, it is curious that apart from these constituents, only aggressiveness showed a significant correlation with stream size and then only at the Main Stream Sink.

Fair Lady Well characteristics while the flow had ceased.

On the day the Pool Outflow dried up (13/08/95), the Fair Lady Well also ceased flowing, leaving a stagnant pool. After previous marked stability, the water temperature at the spring was notably higher than normal; 14.0 °C compared with the mean value of 10.0 °C and Standard Deviation 0.3 °C at the site. Results in Table 3 also showed that concentrations of total hardness, aggressiveness, alkaline hardness, calcium, chloride and potassium were abnormal. As the drought continued, samples from the slowly dropping pool yielded increasingly atypical results. On 24/08/95 sulphate, nitrate and sodium had also become wildly different from normal. Chloride and nitrate concentrations both exceeded 70×10^{-5} M (univalent). It is suspected that on this occasion the water in the pool had been contaminated by urine. These results show very clearly that the properties of the spring are stable only while the spring is producing water and the stability collapsed when flow ceased.

Fair Lady Well took much longer than the Pool Outflow Stream to resume its flow. By 27/09/95, the water level in the spring was higher but not yet high enough to overflow into the Ladywell Stream and water characteristics were still unusual. But whereas total hardness, alkaline hardness and calcium in the now stagnant pool were at first higher than usual, these interrelated quantities were now lower than normal. On 18/10/95 the stream was flowing feebly, and the characteristics were already normal except for aggressiveness. By 7/11/95 the stream was flowing strongly, and all the stream's characteristics were back to normal. No subsequent abnormalities occurred in non-alkaline hardness or sulphate. The fact that the flow of Fair Lady Well took so long to resume is a clear proof that while the well was not flowing, water continued to leave the aquifer. This implies there is at least one other as yet undiscovered point of outflow from this aquifer. It is possible that such an outflow contributes to the source of the present Plantation Inlet Stream in St Cuthbert's Swallet (Stenner, 1997, p18). There must be a supply to the newly located tributary stream and many of the characteristics of the present Plantation Inlet at Plantation Junction are similar to those of Fair Lady Well. The speculated link with a possible extra outflow from the Fair Lady Well aquifer is, therefore, based on real data.

As from 13/08/95 to 18/10/95 (inclusive) no water was flowing from the spring, the data from these dates describe a stagnant pool rather than a flowing spring. These clearly unrepresentative data were deleted from the databases used to generate summaries and figures.

Results from the dry summer in 1996

Sampling of the streams was continued until December 1996, to find out whether there would be a repeat of the 1995 calcium sulphate event following further unusual dry spells in 1996. Several times the flow of the Pool Outflow Stream became very low, but at no time did flow cease and Figure 4 shows that there was no repeat of the 1995 sulphate surge (Heathwaite *et al.* 1999, p256). In 1995, sulphur transformations had taken place within the marshes upstream of the Mineries Pool, which could only take place when the water level in the marsh fell below the normal minimum level. In 1996 there was no fall in the minimum water level, so there was no repeat of the sulphate surge.

Seasonality of water hardness

Atkinson (1971) thought that apparent seasonality in calcium alkaline and total hardness in the former Plantation and St, Cuthbert's streams was possibly a consequence of the seasonality of the normal rainfall pattern. The present data in Figures 3, 8, 13 and 14 show a very great dependence on stream size, hardness being higher in summer than in winter. However, there is a very close inverse relationship between alkaline hardness and stream size (Heathwaite *et al.* 1999, p261, Figure 9) and the possibility that there might be a seasonal factor which was not related to stream size was uncertain until February 1997.

After heavy rainfall in late November and early December 1996, there was an extremely unusually prolonged midwinter dry spell. The streams were sampled in early February 1997, immediately before a heavy rainstorm ended the dry spell. The stream size measurements (91 l/min and 360 l/min at the Pool Outflow and at the Main Stream Sink respectively) were lower than any previous midwinter measurements by either Atkinson or Stenner (comparing present records to the combined stream sizes in earlier records). The total hardness at the cave entrance (146 ppm as $CaCO_3$) was higher than any previous mid-winter value. This value was significantly lower than the summer maxima of about 180 ppm $CaCO_3$ recorded in 1994, 1995 and 1996; but on every occasion when the hardness exceeded the February 1997 value, the stream size had fallen to values smaller than in February 1997. The hardness was, in fact, similar to occasions in midsummer when the stream size had been similar in size. In midwinter, because evapo-transpiration water losses are low, St. Cuthbert's Stream is most unlikely to fall to the extremely low levels at which the hardness rises to the summer maximum values. This factor ensures that, viewing the alkaline hardness/stream size regression equation, it will be extremely unlikely for the winter values of total hardness to rise to the high summer values.

The possibility of a systematic link between temperature, stream size and alkaline hardness was tested further. In St. Cuthbert's Stream near the Entrance, measurements were available for each of the three factors, stream size, water temperature and alkaline hardness, on 65 occasions. The following three regression equations were calculated:

Alkaline hardness = 1006 ($Q^{-0.4}$ + 38.4 $\rho(65)$ = **0.904**

Alkaline hardness = 5.36 (T (water temp) + 61.5 $\rho(65)$ = **0.643**

T (water temperature) = 85.2 ($Q^{-0.4}$ + 3.69 $\rho(65)$ = **0.638**

The significant relationship between water temperature and stream size was to be expected, because it is well known that stream sizes in Britain are very much greater in winter than in summer. Because of the very close relationship between alkaline hardness and stream size, it was inevitable that the correlation between alkaline hardness and water temperature would reflect the close relationship between temperature and stream size; and these two relationships do indeed have co-relationships which are similar in magnitude, and significant. However, the significance of the alkaline hardness/stream size regression equation is very much higher than that of the other two.

The evidence suggests that seasonal effects in the hardness of the surface streams (other than the indirect effect of the seasons on stream size) are limited to an enhancement of total hardness (in extreme low water conditions in dry summers) to approximately 180 ppm as $CaCO_3$.

Seasonality of other water characteristics

Nitrate concentrations in the Pool Outflow and St. Cuthbert's stream (Figure 4) were low from mid-May to late October, and higher from late October or early November to May. In the Fair Lady Well, nitrate concentrations were higher than in the Pool Outflow site and at the Main Stream Sink, but there was an extremely low variability of nitrate at the spring, a feature of many of the results from this spring, with no seasonality. In the Pool Outflow and Main Stream Sink streams, little seasonal trend in sulphate concentrations (Figure 4) could be seen. However, in the Pool Outflow stream, when data from the calcium sulphate event were ignored, there was a threefold increase in sulphate from minima in low flow to maximum values. As previously described, the natural sulphate variability has an unusual dependence on rainfall rather than a stream size or seasonal linkage. Sulphate variability in Fair Lady Well was outstandingly low.

Variations of potassium concentrations at the three sites (Figure 11) showed seasonal trends similar to those of nitrate. Except at Fair Lady Well, where once again variability was very low, concentrations were low in the same summer/autumn months, and higher in the winter/spring months. In St. Cuthbert's stream at the Main Stream Sink, a very short-lived peak of potassium was found in mid to late August in 1994 and 1995. The reason for the peak, which was not found in the Pool Outflow Stream, may be connected with the life cycle of one of the plant species living in or around the stream downstream of the Pool Outflow.

The seasonal variations recorded in nitrates and potassium, both of which are plant nutrients, need further comment. Concentrations of the two species may have been low in summer due to uptake by biological processes. Conversely, the levels may have been higher in winter because of release from decaying vegetation; potassium salts and all nitrates are highly soluble in water and readily leached from decaying organic materials. The data for potassium and nitrate showed the same displacement from astronomical mid-summer and mid-winter as temperature measurements. This displacement is a common phenomenon, frequently found in biological studies and, for example, coastal marine temperatures. It was suspected in temperature variations in inlet streams in St. Cuthbert's Swallet (Stenner, 1968).

Other ions present in the streams

IC results failed to detect the presence of fluoride, phosphate, bromide, iodide, or any other anions other than those which were determined. In one polluted sample, from Fair Lady Well, 24/08/96, during the time when there was no flow from the spring, there was a considerable ion imbalance. The authors suspected there was an ammonium ion concentration of approximately 93×10^{-5} M (Knights and Stenner, 1999, p246). However, recent colorimetric determinations of ammonium levels in a large number of water samples from a variety of streams on Mendip revealed ammonium levels which were in every case lower than 1 mg l^{-1} (Knights and Stenner, *in prep.*). Previous work (Stenner, 1977) showed that the levels of heavy metals present in the streams would be too low to influence the anion/cation balances of this study.

The detection limit for phosphate and fluoride by IC used here is lower (by a factor of more than 10) than in available colorimetric methods. The present method would have detected levels high enough to affect anion/cation balances, and would have revealed any gross contamination.

Nitrate

In earlier studies of a selection of samples from cave streams, which yielded good ion balances (but with no direct measurement of nitrate), it was concluded that nitrates in those waters were present in concentrations too low to be detected by the methods available (Stenner, 1971, p285). By using IC in the present study, the nitrate levels in the streams have been reliably quantified. Data from 1968 to 1970 were re-examined. During this period, 4 samples from the Pool Outflow stream at Plantation Swallet, and 4 samples from the former St. Cuthbert's stream close to the Main Stream Sink were analysed for sulphate, chloride and total anion concentrations. Anion/cation balances for the 8 samples were satisfactory. In these examples, total anion - (chloride + sulphate) provided estimates of the nitrate concentrations, summarised in Table 5.

Site	No	Mean	S.D.
Pool Outflow Stream, Plantation Swallet	4	4.4	2.1
St. Cuthbert's Stream, St. Cuthbert's Swallet	4	0.9	4.2

Table 5. *Nitrate concentrations in streams feeding St. Cuthbert's Swallet in 1968 and 1969, estimated from analyses for total anion content, chloride and sulphate concentrations. All concentrations are expressed as* $10^5 \times M$ *(univalent).*

The estimates for nitrate concentrations shown in Table 5 do not differ (at the p=5% level) from the present data for the Pool Outflow stream (Table 1) or the former St. Cuthbert's stream.

The conclusion is that in these two streams, there has been no statistically significant change in nitrate concentrations between 1969 and the present time. In this respect, the water at all three sites is unlike that at two major Mendip risings, Wookey Hole and Cheddar, where there is evidence of considerable contamination by nitrates, and where nitrate concentrations have risen considerably since 1968 (Chapman *et al.* 1999).

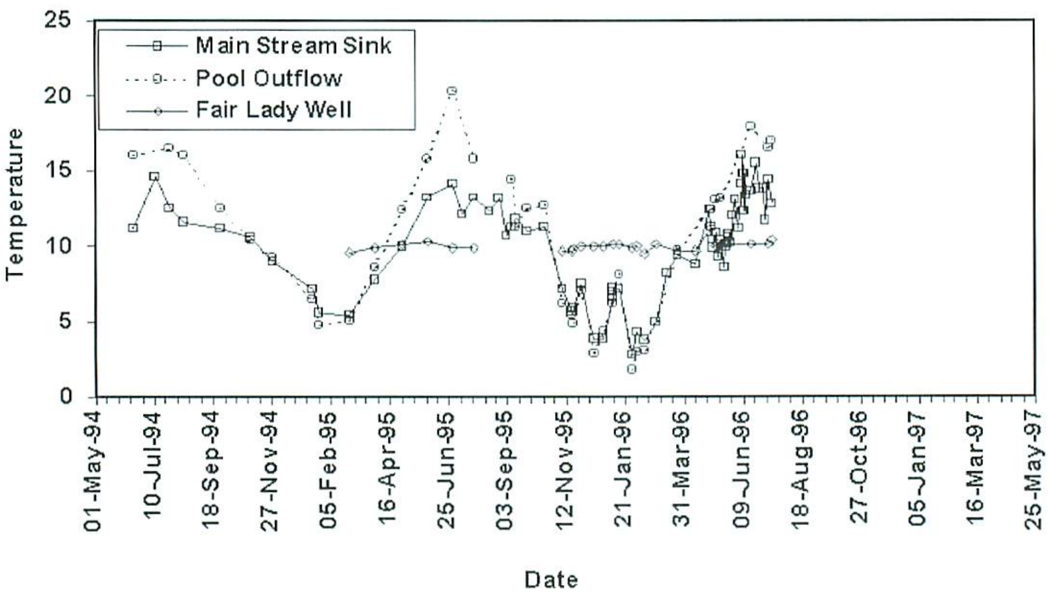

Figure 2. *Temperature °C, at three stream sites, May 1994 to February 1997.*

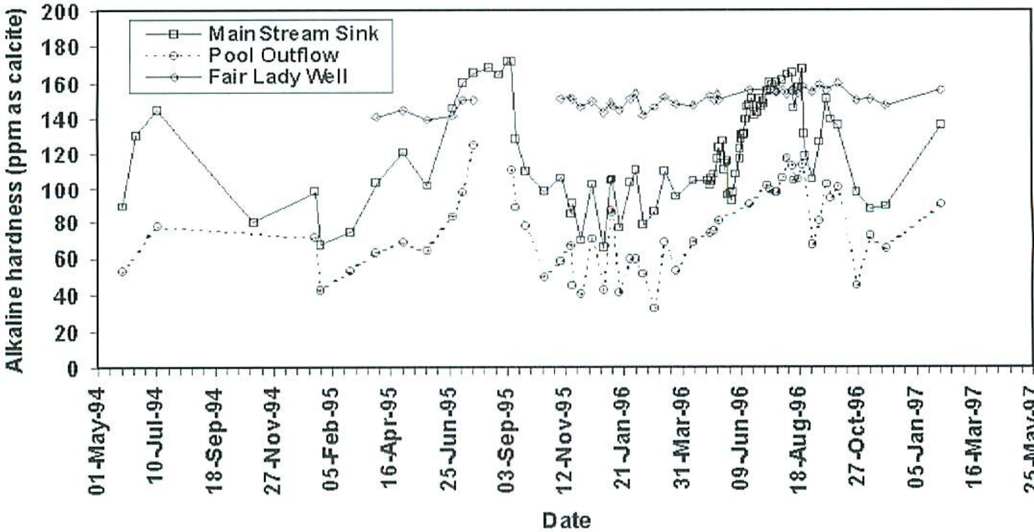

Figure 3. *Alkaline hardness, ppm as calcite, at three stream sites, May 1994 to February 1997.*

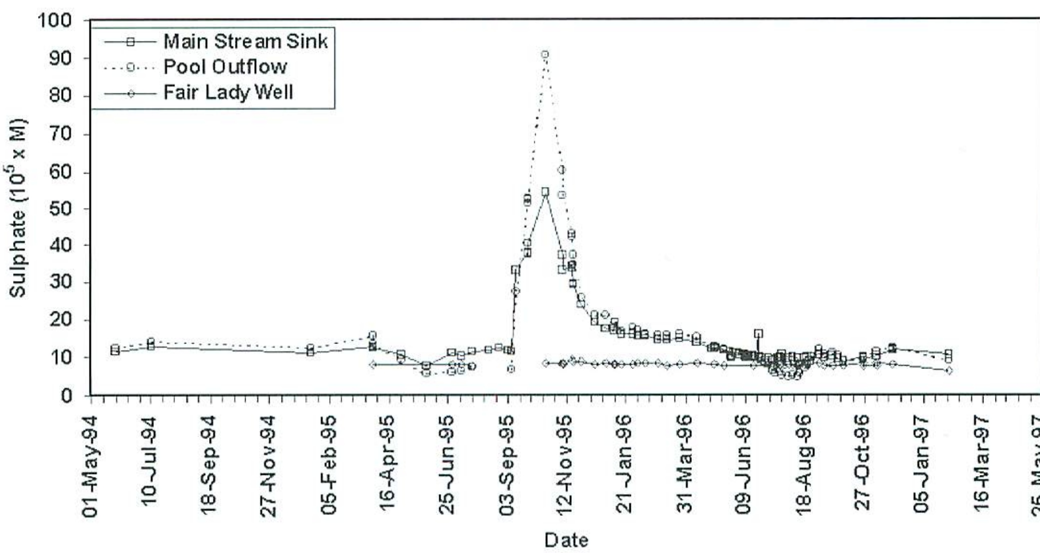

Figure 4. *Sulphate concentrations at three stream sites, May 1994 to February 1997.*

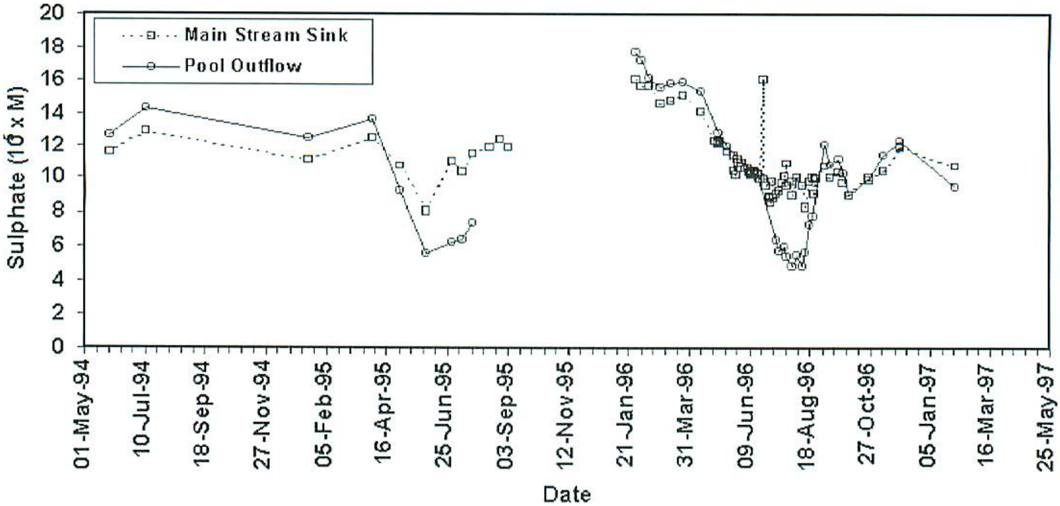

Figure 5. *Sulphate concentrations at two stream sites, May 1994 to February 1997, excluding data from the calcium sulphate surge.*

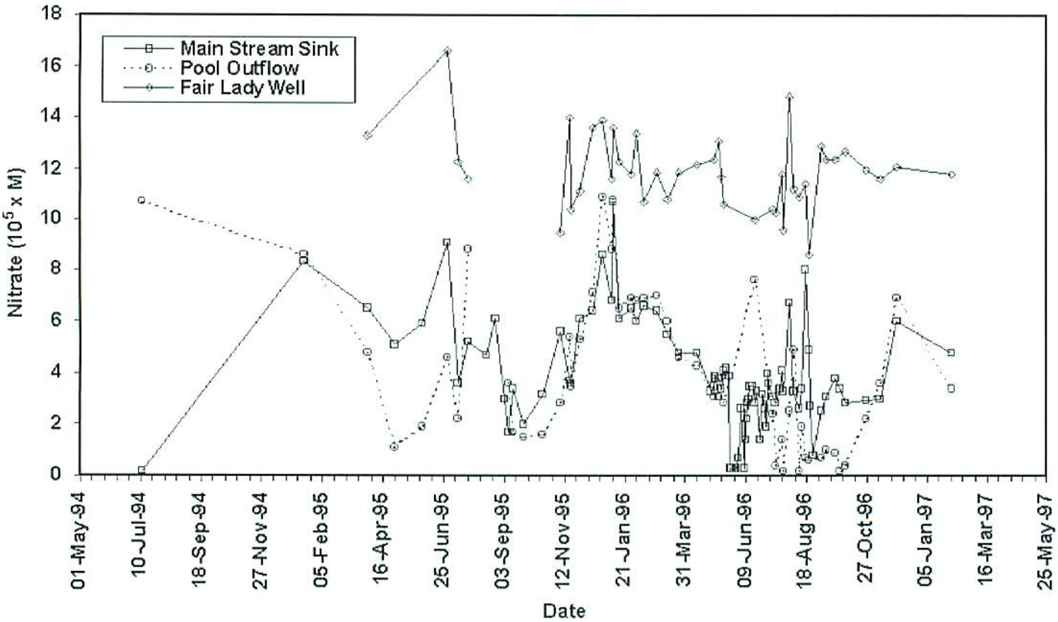

Figure 6. *Nitrate concentrations at three stream sites, July 1994 to February 1997.*

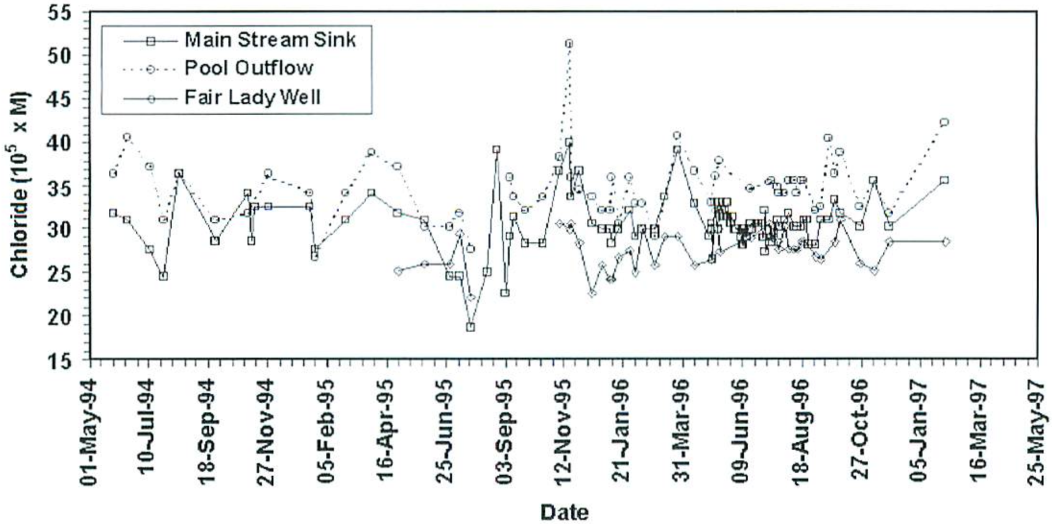

Figure 7. *Chloride concentrations at three stream sites, May 1994 to February 1997.*

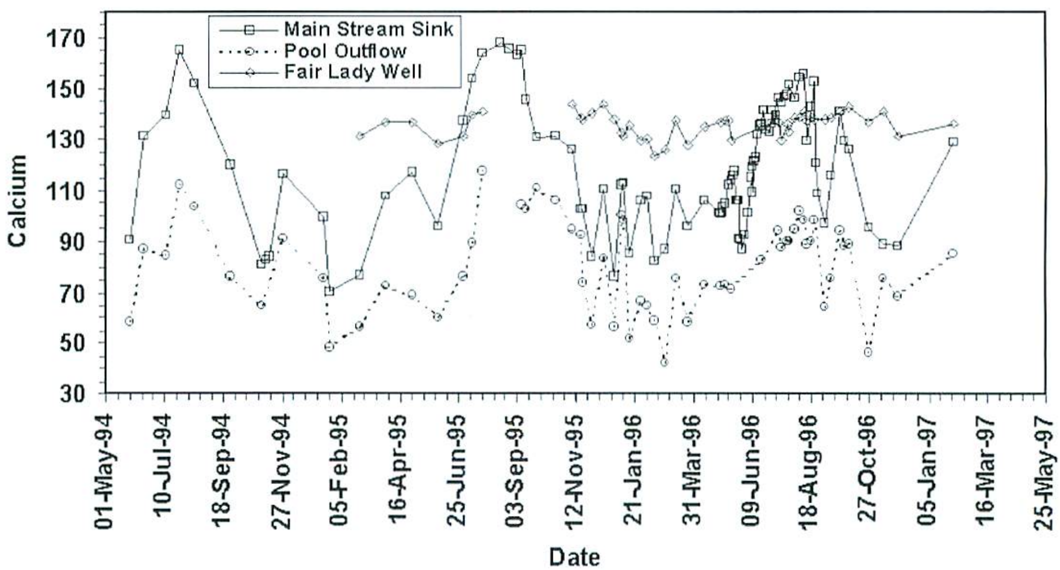

Figure 8. *Calcium concentrations, ppm as calcite, at three stream sites, May 1994 to February 1997.*

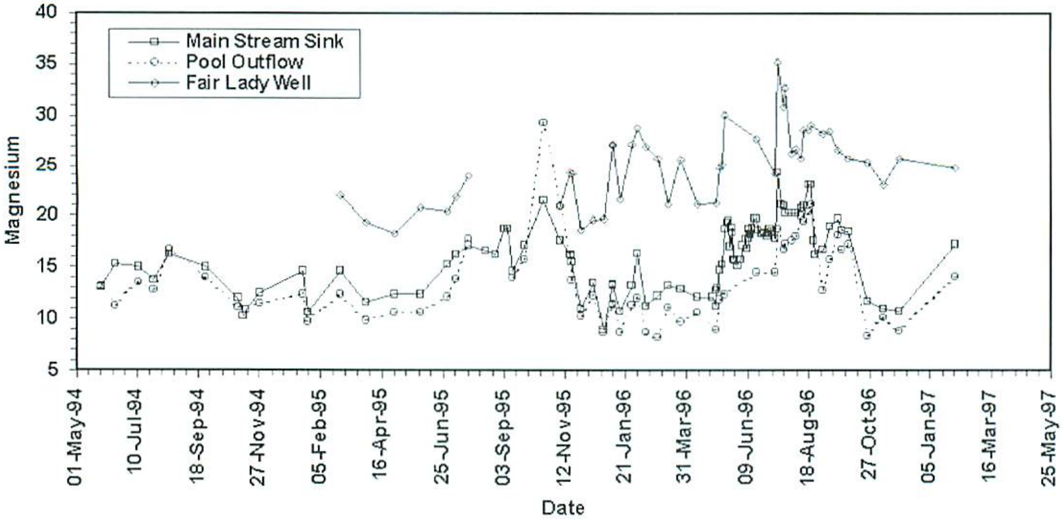

Figure 9. *Magnesium concentrations, 10^5 x M, at three stream sites, May 1994 to February 1997.*

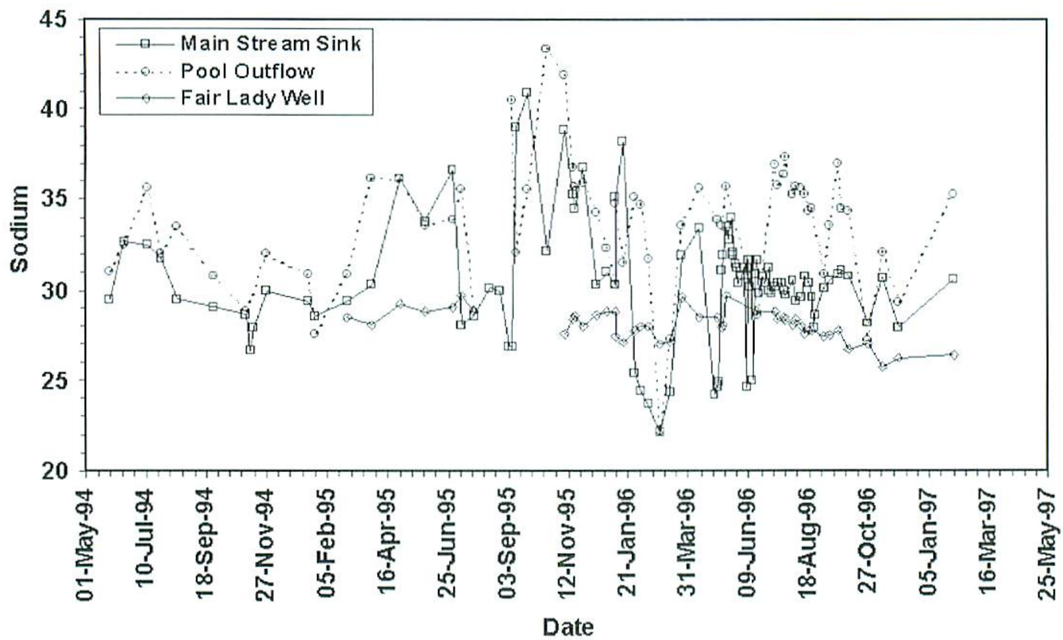

Figure 10. *Sodium concentrations, 10^5 x M, at three stream sites, May 1994 to February 1997.*

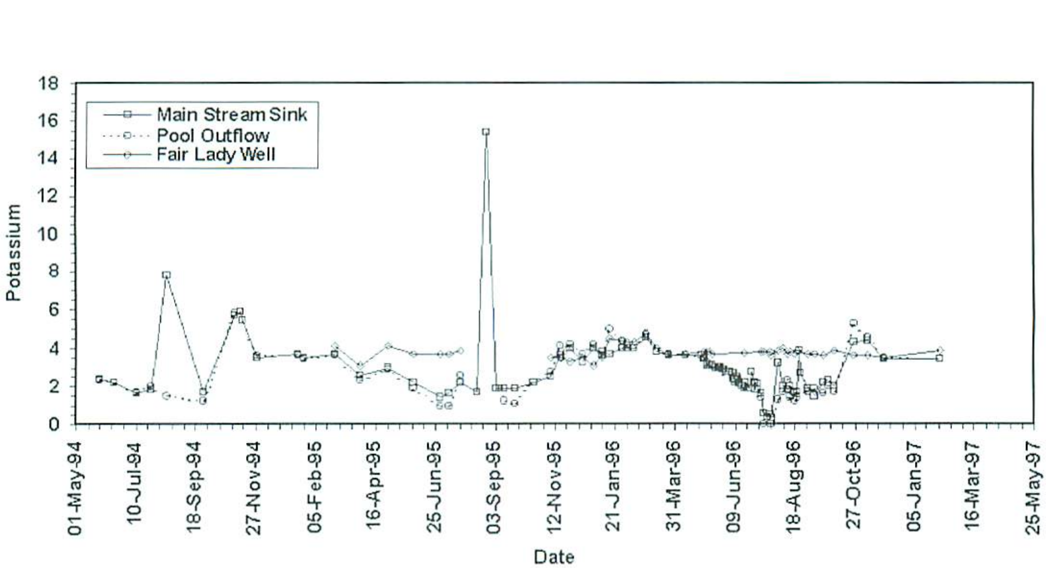

Figure 11. *Potassium concentrations, 10^5 x M, at three stream sites, May 1994 to February 1997.*

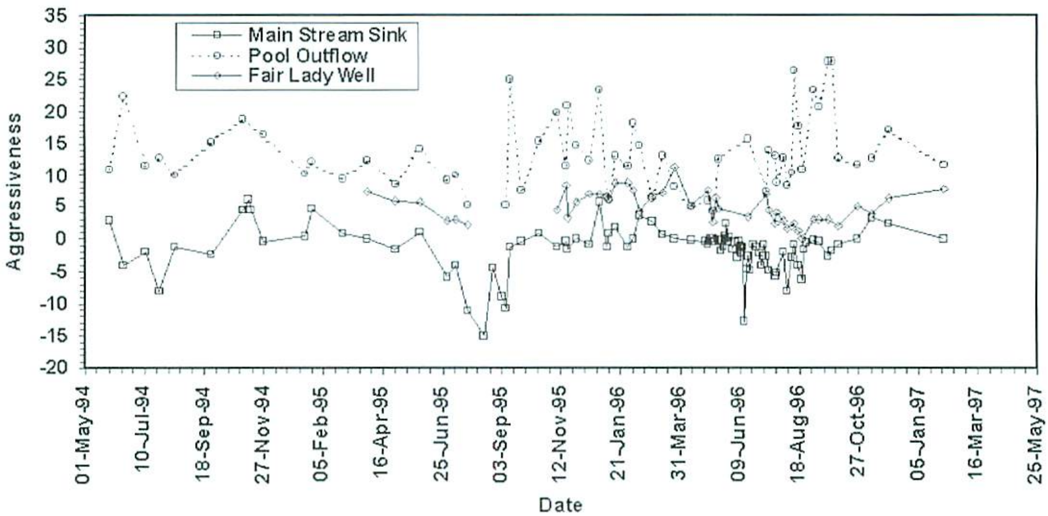

Figure 12. *Aggressiveness to calcium carbonate, ppm as calcite, at three stream sites, May 1994 to February 1997.*

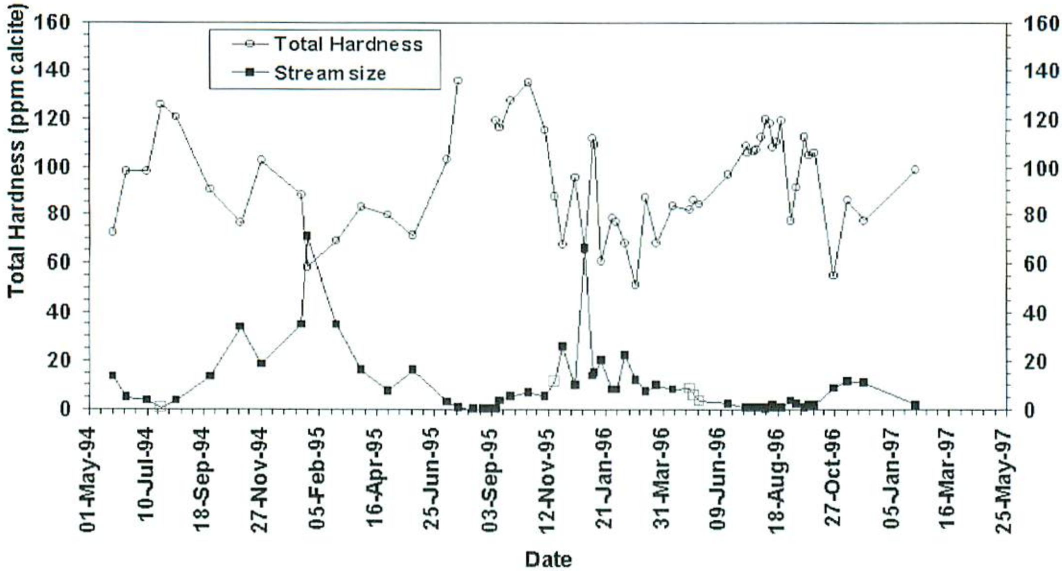

Figure 13. *Total hardness (ppm as calcite) and stream size (in litres per second) at the Mineries Pool Outflow Stream, May 1994 to February 1997. (The stream sizes at the five points marked as open boxes are estimates, the salt dilution measurements having failed).*

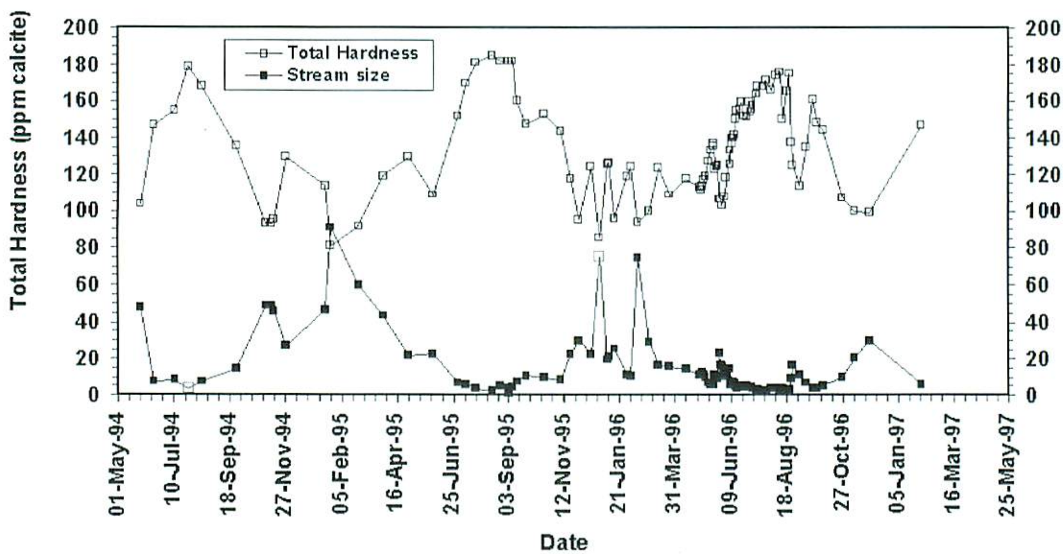

Figure 14. *Total hardness (ppm as calcite) and stream size (in litres per second) at St Cuthbert's Stream, Main Stream Sink, May 1994 to February 1997. (The stream sizes at the two points marked as open boxes are estimates, the salt dilution measurements having failed).*

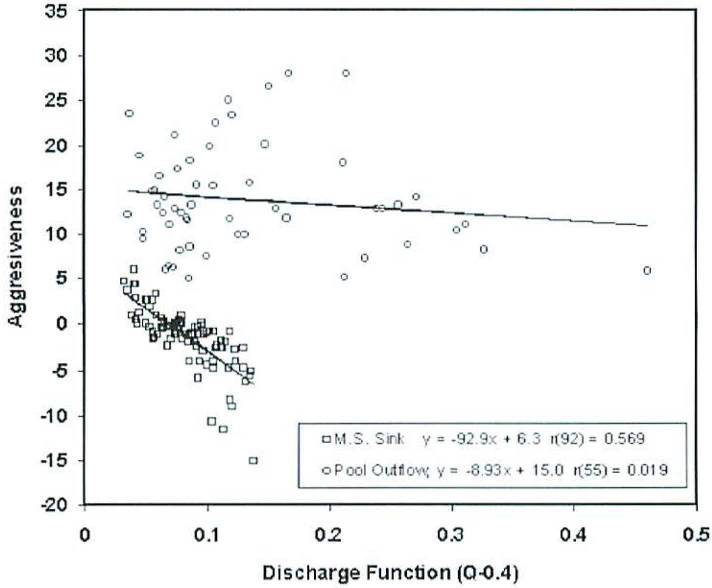

Figure 15. *The relationship between aggressiveness to calcium carbonate (ppm as calcite) and Discharge Function($Q^{-0.4}$) at St. Cuthbert's Stream, Main Stream Sink and the Mineries Pool Outflow.*

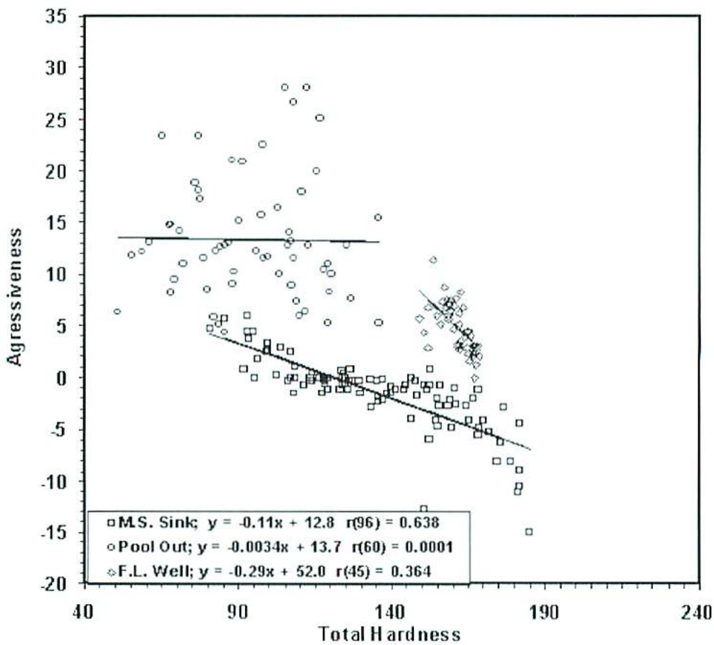

Figure 16. *The relationship between aggressiveness to calcium carbonate (ppm as calcite) and total hardness (ppm as calcite) at three stream sites, May 1994 to February 1997.*

CONCLUSIONS.

Many of the characteristics of the Fair Lady Well showed a variability which was outstandingly low, especially when considering those of the nearby Mineries Pool Outflow Stream. They included temperature, total calcium and alkaline hardness, sodium, potassium, sulphate and aggressiveness.

The unusually low variability of most ions in Fair Lady Well explains why no seasonal patterns of variations, or any inter-species correlations were found at the site.

At the Pool Outflow and the Main Stream Sink, only temperature, potassium and nitrate showed seasonal variability. At these two sites, sulphate showed elevated levels after the first heavy rain following a prolonged dry spell.

At the Pool Outflow and the Main Stream Sink, total calcium and alkaline hardness showed a high variability, being inversely related to stream size. There was no seasonal pattern, apart from an indirect seasonal aspect of stream size, the result of seasonal patterns of rainfall. Although the regression between alkaline hardness and the Discharge Function ($Q^{-0.4}$) had a very high correlation coefficient, there were instances when the total hardness was higher or lower than expected, for reasons which are not yet clear.

Aggressiveness, and then only at the Main Stream Sink, was the only other quantity to show a dependence on stream size.

After a highly unusual summer drought in 1995, when the water level in the Mineries Pool fell to about 1.5 m below the normal base level in very high temperatures, a huge pulse of calcium sulphate passed through the pool to St. Cuthbert's Swallet. After another intense drought in 1996, when the water level in the Mineries Pool did not fall below the normal base level, there was no calcium sulphate surge. This suggests that a partial drying out of the marsh played a part in the genesis of the calcium sulphate surge.

When the pool outflow ceased in 1995, flow from Fair Lady Well stopped. After the Pool Outflow Stream restarted, it took more than another month for flow from the spring to restart. This suggests that the aquifer has a second outlet at a lower level, which has not yet been located. It may be connected with the recently discovered complex of hidden streams near the Maypole Overflow Corner.

Nitrate concentrations at the pool outflow stream and at the Main Stream Sink were low, and indistinguishable (statistically) from those found in samples from the two sites in 1968 and 1969.

Ion Chromatography has proved to be a very reliable technique in the study of the sulphate event in the Mineries Pool Outflow stream. In this study, the reliable and accurate determination of anions in the samples provided by this tool made a very important contribution in enabling a precise description of the event to be made. Ion chromatography proved to be substantially quicker and more accurate than the colorimetric method previously used for sulphate.

ACKNOWLEDGMENTS

Grateful thanks are due to Mrs F.L. Stenner who assisted both in carrying out routine salt dilution measurements and in the surveying of the surface streams feeding St. Cuthbert's Swallet.

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