# A CALCIUM SULPHATE SURGE IN A STREAM DRAINING AN UPLAND MARSH ON MENDIP (SOMERSET) FOLLOWING THE DROUGHT IN THE SUMMER OF 1995.

by

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## ABSTRACT

During a drought of historic proportions in 1995, the Mineries Pool Outflow stream (the largest stream entering St. Cuthbert's Swallet) and a nearby spring stopped flowing. The Pool is supplied by water draining an upland marsh in an area that has seen more than 1600 years of lead mining and lead smelting. When flow of the Pool Outflow resumed, a huge surge of calcium sulphate appeared in its water. From a mean concentration of $10.1 \times 10^{-5}$ M, and a previous maximum of $17 \times 10^{-5}$ M, in 40 days the sulphate concentrations rose to $91 \times 10^{-5}$ M. The event lasted approximately 140 days. In 1996 there was another severe drought, but the streams did not dry up, and the sulphate levels remained normal. Ion chromatography was used to determine sulphate and nitrate concentrations in the streams. The survey was an example of the application of a scheme of analysis developed by Knights and Stenner, in which ion balances were used to analyse the reliability of the analytical data.

## INTRODUCTION

In the summer of 1995, a survey was being made of selected hydro-chemical character-istics of upland streams that enter St. Cuthbert's Swallet cave system, and resurge as part of the River Axe at Wookey Hole Cave. During a drought of historic severity, the outflow stream of the Mineries Pool stopped flowing, a very unusual event, and the water level in the pool contin-ued to fall. Water levels fell below the minimum level of the pool, lowering the water levels in the marshes upstream of the pool. A sulphate surge, the subject of this paper, began soon after the outflow of the stream resumed.

*A description of the study area*

The location of the sites is shown in Figure 1. Three sites (1: Mineries Pool Outflow Stream; 2: Main Stream Sink of St. Cuthbert's Stream and 3: Fair Lady Well) were studied. Site 3, which is 23 m from the Mineries Pool, provided important data for comparison with those from Sites 1 and 2.

The catchment area of St. Cuthbert's Swallet has been described elsewhere (Stenner, 1997). The rock underlying North Hill, the south-western part of Stock Hill and the valley floor upstream of the Mineries Pool is Old Red Sandstone (Green and Welch, 1965). The sub-soil above the bedrock, although largely derived from the underlying bedrock, has been extensively changed by at least seventeen centuries of lead mining and lead smelting (Gough, 1962). Ore-bearing rocks from the Stock Hill ore-field and from surrounding areas were transported to the valley, where the streams were used to separate the ore from the residues, which were discarded in the valley.

There were areas of marsh in the valley in pre-Roman times (Balch, 1914). Extensive areas of marsh presently occupy the sites of former reservoir pools in the valley. Two reservoir pools at the Chewton Minery were already in use in 1860, before the Mineries Pool was constructed. The present Mineries Pool is a remnant of what had been a considerably larger
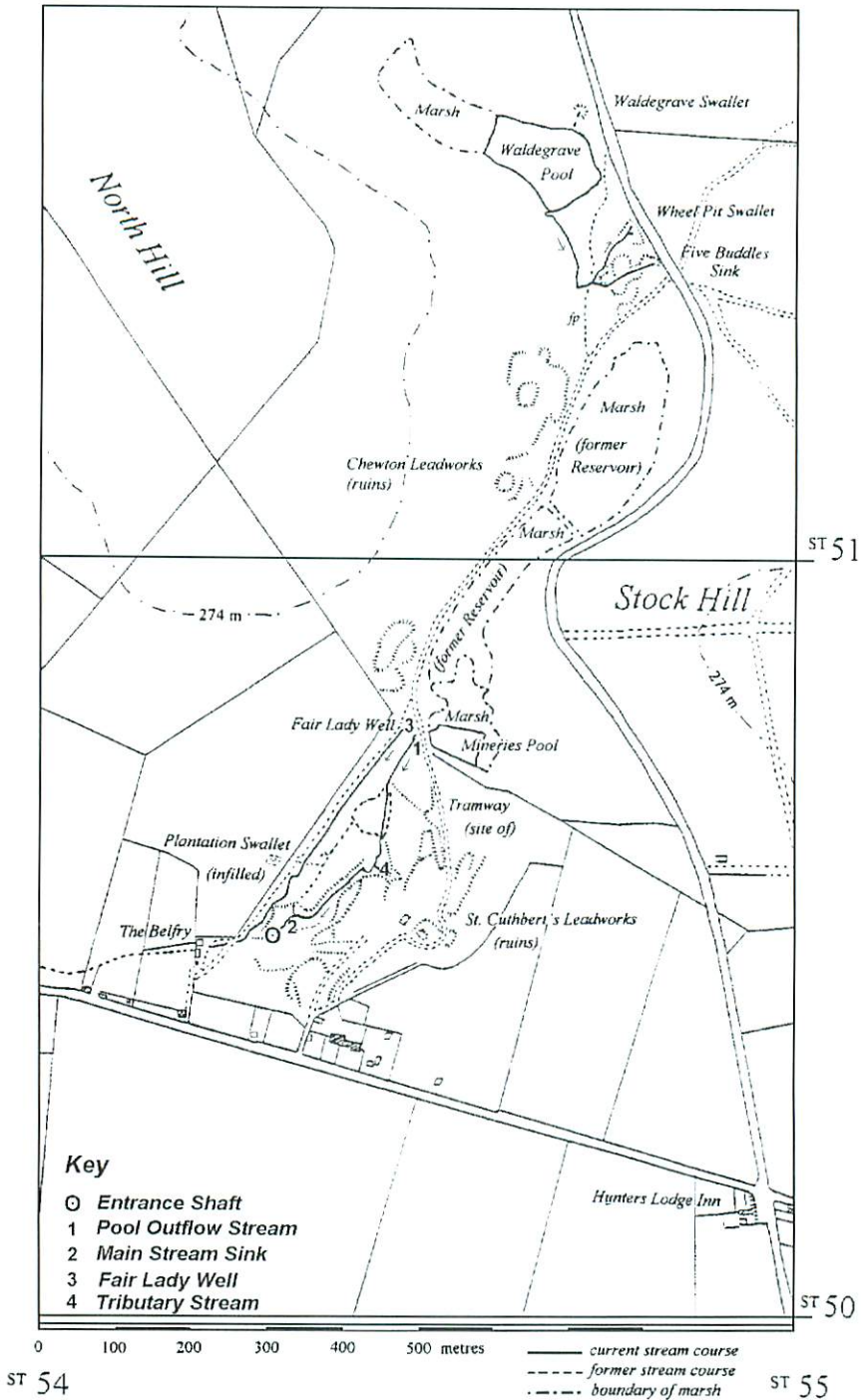
**Figure 1.** *Area map: Streams draining to St Cuthbert's Swallet, Somerset.*
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pool, the majority of which has been colonised by marsh-creating vegetation. Most of the water from the catchment area of St. Cuthbert's Swallet passes through the Mineries Pool.

## EXPERIMENTAL PROCEDURES

Throughout the period of the present study, concentrations of all ions present in significant quantities were determined, to enable the precision of the analyses to be quantified by calculating ion balances. Full details of sampling and analytical procedures and using ion balances to examine overall analytical reliability are available elsewhere (Knights and Stenner, 1999). Duplicate samples for measuring aggressiveness were saturated with AnalaR $CaCO_3$ at the site. On every occasion when the stream could be seen to be carrying sediment, the sample was filtered at the time of collection. Samples were kept cool and in the dark until analysed. Samples were collected and stored in 250 ml or 130 ml plastic bottles, except for those collected for measuring aggressiveness, which were collected in 67 ml bottles. Analyses for total hardness, aggressiveness and alkalinity were completed within 24 hours of collection.

Water temperatures were measured throughout the calcium sulphate surge, using either a calibrated electronic or a mercury-in-glass thermometer, both of which were graduated to 0.1°C. The discharge of the Pool Outflow stream and St. Cuthbert's Stream (close to the stream sink) were measured by salt dilution, using a simple constant flow apparatus and standard KCl solutions (Stenner and Stenner, *in prep.*). In many of the regressions involving discharge (Q) that were investigated, the power function $Q^{-0.4}$ was used.

### Anion analyses

Nitrate and sulphate levels were determined using ion chromatography. Concentrations were calculated as mg $l^{-1}$ and then converted to Molar concentrations. Bicarbonates were determined (as alkaline hardness) by titrating 25 ml aliquots with standard 0.02 M HCl, using BDH 4.5 indicator. Silver nitrate titrations (using 25 ml aliquots) were used for chloride analyses. Ion chromatography (IC) would have detected the presence of many other ions, notably fluoride, phosphate, bromide or iodide. If these ions had been detected, their concentrations would have been determined by IC, but in the event, none were detected.

### Cation analyses

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

### Units

All concentrations were expressed as $10^5 \times$ Molarity (the unit appropriate for the investigation of ion balances).

## ACCURACY AND PRECISION

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

Total hardness, calcium and aggressiveness to $CaCO_3$, 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. The overall analytical reliability was assessed by making ion balance calculations (full details in Knights and Stenner, 1999).

## A DESCRIPTION OF THE CALCIUM SULPHATE SURGE

In the severe drought in 1995, the Pool Outflow stream stopped flowing on 13 August 1995. This is a very rare event. Mosses in the pipe in the dam at the outlet from the Mineries Pool were still waterlogged so flow had probably ceased that day. As the drought continued, the water level in the Mineries Pool continued to fall for two weeks when daytime temperatures were unusually high, to extremely unusually low levels (approximately 1.5 m below the normal minimum level; possibly the lowest level since the pool was first created). When heavy rain came at the end of August, the water level in the pool rose steadily, but by 3 September 1995 there was still no outflow. On 8 September 1995, the first very small outflow (7.0 l/min) was sampled (the water chemistry was normal), and by 13 Sptember 1995, the outflow stream was much bigger (213 l/min), and the first sign of the developing sulphate surge was noticed.

While the pool outflow was dry, the seepage contribution to St. Cuthbert's Stream (which had been the entire St. Cuthbert's Stream before the Pool Outflow stream changed its course, see Stenner, 1997) continued to flow. At no time did the stream at the cave entrance dry up. Since the Pool Outflow is now (except in extreme low-water conditions) the largest source of St. Cuthbert's Stream, any unusual chemical events in the Pool Outflow stream would have an effect on the chemistry of St. Cuthbert's Stream.

Time series graphs for non-alkaline hardness and sulphate, Figures 2 and 3, show the calcium sulphate event. When the Pool Outflow stream started to flow again on 8 September 1995 (following about 26 days when there was no flow), the concentrations were very similar to those before flow had ceased. On 13 September 1995, after a further 5 days, it was noticed that the non-alkaline hardness was higher than normal. But on 27 September 1995, after 14 more days, non-alkaline hardness was twice as high as any previously recorded value, and an unusual event was seen to be in progress. The event reached a maximum on 18 October 1995, after a further 21 days (i.e. a total of 40 days after flow restarted). The fall in non-alkaline hardness was more gradual than the rise had been, and levels remained abnormally high 88 days after the peak, giving the event a total duration of 128 days, more than four months.

Results from St. Cuthbert's Stream at the Main Stream Sink (Site 2) confirmed the details of this event. Non-alkaline hardness at the site remained normal when the Pool Outflow stream was dry. During the surge, the stream at the sink had the non-alkaline hardness of the Pool Outflow stream, diluted by the seepage stream with normal non-alkaline hardness. This explanation was confirmed by applying stream ratio calculations to the changes observed between Site 1 and Site 2, and by the chemistry of the stream at the sink while there was no Pool Outlet stream. Both sets of data showed that the chemistry of water seeping from the marsh near the tramway and joining the Pool Outflow stream was similar to the chemistry of the former St. Cuthbert's Stream, as determined by both Stenner and Atkinson (Stenner and Stenner, *in prep.*).
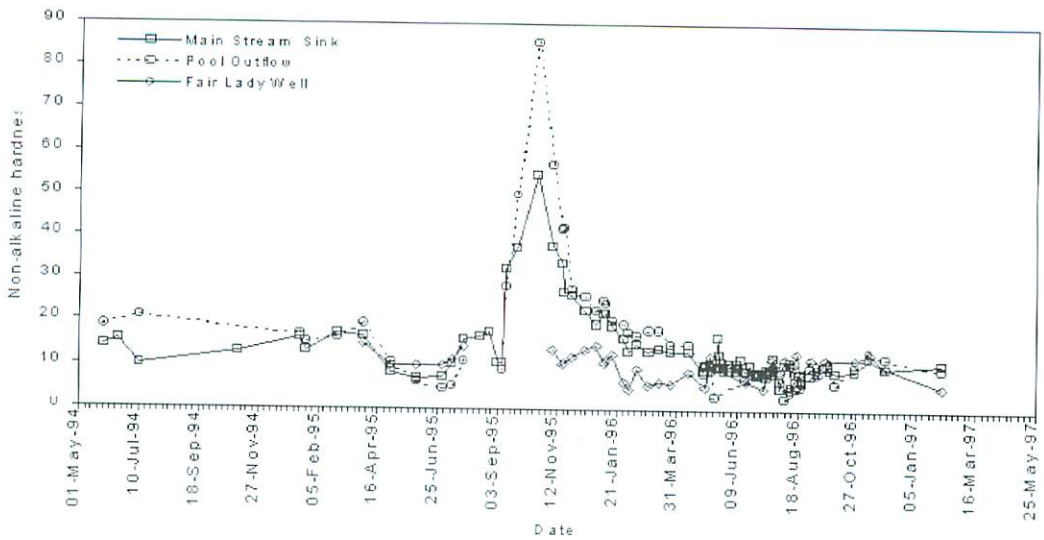
**Figure 2.** *Non-alkaline hardness, ppm calcite, at three stream sites,
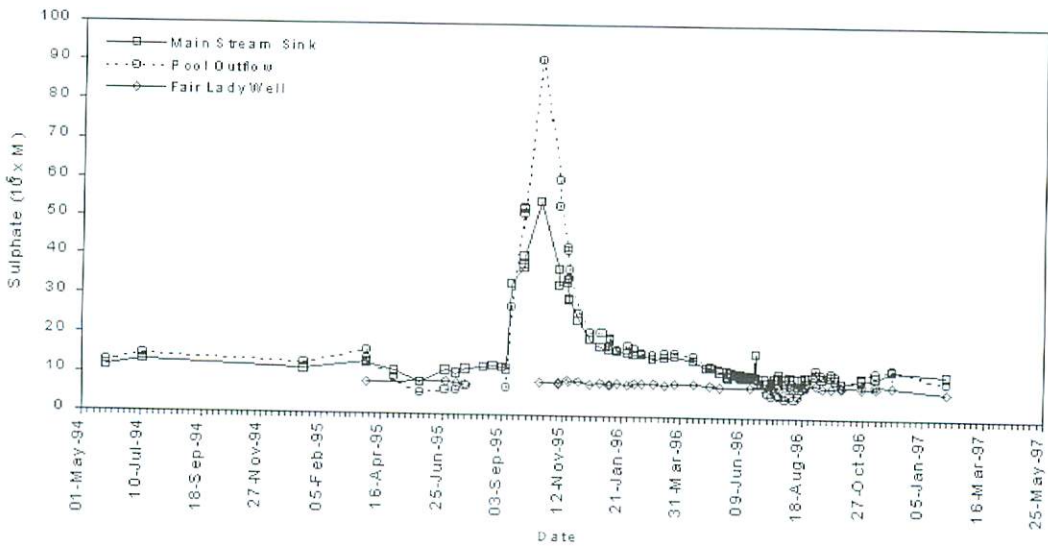May 1994 to February 1997.*

**Figure 3.** *Sulphate concentrations at three stream sites, May 1994 to February 1997*

In particular, the data showed that the water in the former St. Cuthbert's stream had absolutely no enhancement of non-alkaline harness or sulphate. This water, therefore, had never flowed through the Mineries Pool, as Irwin has stated (Irwin, 1991).

At Sites 1 and 2, the time series graphs for non-alkaline hardness and sulphate were remarkably similar in shape to each other (Figures 2 and 3). In addition, at the Pool Outflow a simple linear 1:1 regression between sulphate and non-alkaline hardness was found, with a very high correlation coefficient; see Figure 4. An extremely similar regression was found at the Cave Sink. This proved conclusively that in this event, the non-alkaline hardness was caused by sulphate ions. Although levels of magnesium, sodium and chloride were higher than usual in the samples collected at the peak of the event, other ion concentrations remained normal and the levels of magnesium, sodium and chloride were normal before and after the peak of the surge. The event was, therefore, overwhelmingly restricted to abnormally high values of non-alkaline hardness and sulphate. The anion/cation balances during the event were good, precluding the possibility that any ion (other than those that were determined) may have been involved in the event. Aggressiveness data proved that no free sulphuric acid was present. It follows that the sulphate in the event was calcium sulphate and that the event was a surge of dissolved calcium sulphate.

The scheme of analyses evolved by Knights and Stenner, backed up by ion balance checks, had been applied to what had originally been seen as some unusual non-alkaline hardness data. Its application had successfully determined the precise nature of the surge, and created the opportunity to examine in detail the nature of interrelationships between the various ions during this highly unusual event.

At the peak of the event, the concentration of sulphate in the Pool Outflow stream was so high that the solubility product of calcium sulphate at 25°C would have been exceeded as a result of further increases of either ion. Although the frequency of sampling makes it statistically possible that there could have been a considerably higher peak within a week or so either side of 18 October 1995, the proximity of the results for that date to the solubility product for calcium sulphate makes this eventuality a chemical impossibility.

The highest values of chloride and sodium concentrations recorded in the Pool Outflow Stream coincided with the peak of the sulphate surge, on 18 October 1995. The figures for chloride and sodium from 18 October 1995 were $43.4 \times 10^{-5}$ M and $43.4 \times 10^{-5}$ M respectively. These figures are compared with the mean, no. (in brackets) and S.D. of $34.7 \times 10^{-5}$ M, (47), $3.4 \times 0^{-5}$ M for chloride, and $33.2 \times 10^{-5}$ M, (47), $3.4 \times 10^{-5}$ M for sodium.

*Results in the dry summer of 1996*

In the summer of 1996 there was another severe drought, which had a duration longer than that of 1995. Sampling of the streams was continued until December 1996, to find out whether there would be a repeat of the 1995 calcium sulphate event. Several times the flow of the Pool Outflow stream became very low (13 July, 3 August, 21 August and 20 September), but at no time did the flow cease. Figure 3 shows that there was no repeat of the 1995 event. Intermittent partial blocking of the dam at the outflow of the pool had been in place, and this conserved the water in the pool. This obstruction changed the discharge hydrograph of the pool outflow stream in 1996, compared with that in 1995. The percentage contribution of the Pool Outflow stream to the stream at the Main Stream Sink also decreased while the blockage was in place.
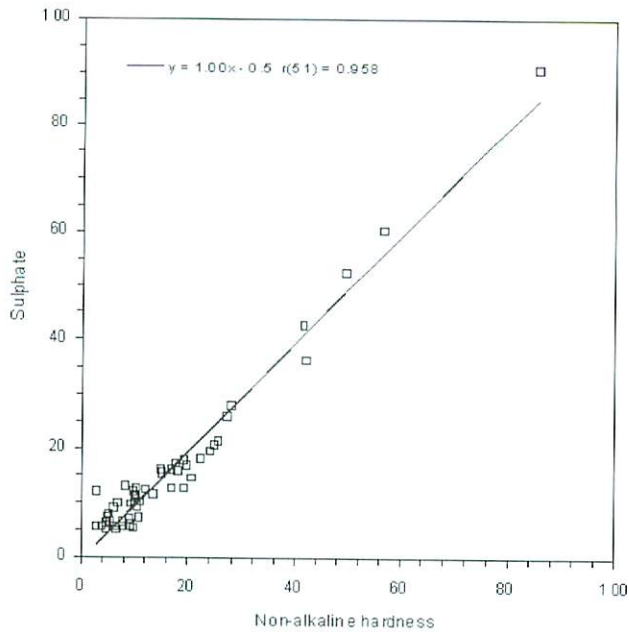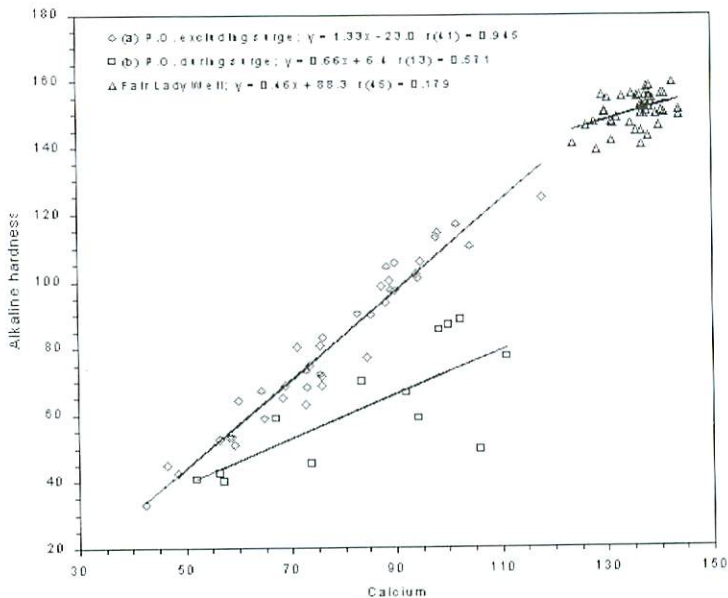
**Figure 4.** *The relationship between sulphate concentrations ($10^5$ x M) and non-alkaline hardness (ppm calcite) at the Mineries Pool Outflow, May 1994 to February 1997.*
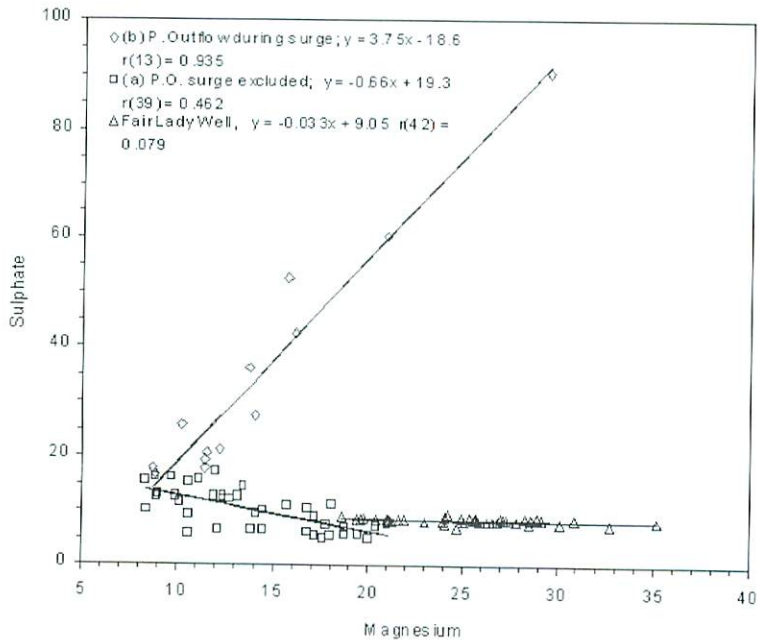


**Figure 5.** *The relationship between sulphate and magnesium concentrations ($10^5$ x M) at the Mineries Pool Outflow (a) before and after the calcium sulphate surge, (b) during the surge and at Fair Lady Well.*
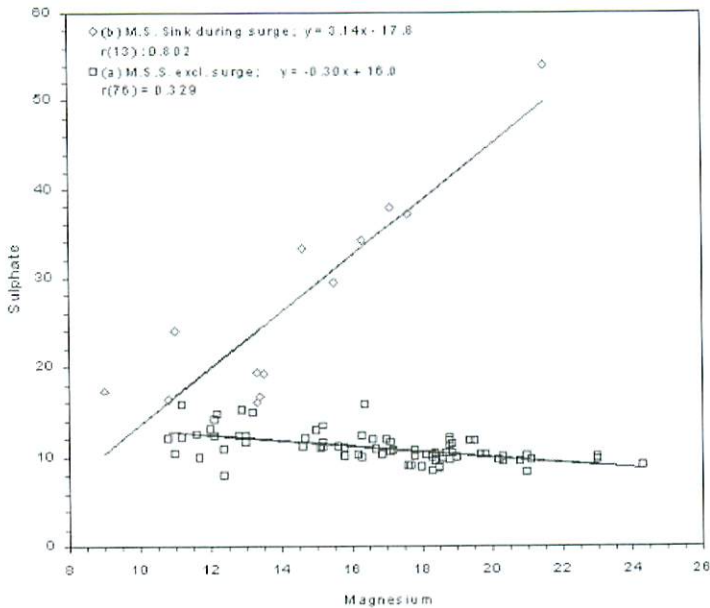
**Figure 6.** *The relationship between sulphate and magnesium concentrations ($10^5$ x M) at St. Cuthbert's Stream Sink (a) before and after the calcium sulphate surge and (b) during the calcium sulphate surge.*



**Figure 7.** *The relationship between alkaline hardness and calcium concentrations (ppm calcite) at the Mineries Pool Outflow (a) before and after the calcium sulphate surge and (b) during the calcium surge and at Fair Lady Well*

The complete absence of any abnormality in sulphate levels following the severe drought in 1996 was a very striking result, which will be discussed below.

## DISCUSSION OF THE RESULTS

1.  INTERRELATIONSHIPS BETWEEN SITE CHARACTERISTICS DURING THE CALCIUM SULPHATE SURGE

*(a) The relationship between magnesium and sulphate*

The interrelationship between magnesium and sulphate in the Pool Outflow stream was examined after separating the data from the surge (13 September 1995 to 15 January 1996), and plotting the two data sub-sets separately. The extraordinary relationship is shown in Figure 5. This remarkable graph is discussed in more detail below. The conclusion is that although magnesium sulphate was only a minor component in the calcium sulphate event, the effect of the surge on the magnesium/sulphate relationship during the surge was extremely striking. There was an extremely similar regression at the Main Stream sink, shown in Figure 6.

*(b) The interrelationships between alkalinity, calcium and total hardness*

In limestone waters alkaline hardness, calcium and total hardness share the same origin (the solution of limestone with a high percentage of calcium carbonate in water containing dissolved carbon dioxide), so all three quantities share similar relationships with each other, and with other common factors such as discharge. Consequently, there is normally a simple close relationship between calcium and alkalinity at a site. At the Pool Outflow site and the Main Stream sink, data from the surge were once more separated in the data set, and the two sub-sets were plotted separately (Figures 7 and 8). Once again, the results are extraordinary, and unprecedented in karst studies on Mendip. The graphs show clearly that during the calcium sulphate surge, the extra calcium sulphate disrupted the normal calcium/alkaline hardness relationship at both sites.

*(c) The interrelationships of alkalinity, calcium and total hardness with discharge*

The distortion of the normal calcium/alkalinity relationships at both sites had an unexpected consequence. At each site, the alkalinity/discharge regression was compared with that for total hardness/discharge and with that for calcium/discharge. The correlation coefficients for the alkaline hardness/discharge regressions were higher at the Main Stream Sink and at the Pool Outflow (0.838 and 0.639 respectively) than those for total hardness/discharge (0.781 and 0.381 respectively) and calcium/discharge (0.719 and 0.369 respectively). At first sight, this result seems to be contrary to the opinions of Knights and Stenner. They supported earlier suggestions (Stenner, 1969) that the alkalinity determination is considerably less reliable than the total hardness (and hence calcium) determination. The explanation is that the distortion of the calcium/alkalinity relationship during the surge had produced a distortion of the normal calcium/discharge and total hardness/discharge relationships. The "rogue" points on the regression graphs for total hardness/discharge and calcium/discharge, which result in lower correlation coefficients, are from the surge. Indeed, these points are not "rogue", but consequences of a real effect, that altered the normal relationships during the surge. The alkaline hardness/discharge

regression was unaffected by the surge and quite independent of it. Data points from the surge do not stand out as apparently "rogue" points on the graph (Figure 9). The fact that the surge was completely unconnected with the normal alkalinity/discharge relationship, and had no effect whatsoever on it, is a strange and completely unexpected discovery.

*(d) The relationship between magnesium and total hardness, alkalinity hardness and calcium*

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, shown in Figure 10 was chosen because alkaline hardness was, apparently, unaffected be the calcium sulphate surge). The relationships must reflect the Ca:Mg ratios in the limestones being dissolved.

## 2.        RELATED OBSERVATIONS AT FAIR LADY WELL

The spring is very close to the Mineries Pool and, like the pool, it stopped flowing (possibly on the same day), during the drought in 1995. However, there was no evidence of any abnormality in sulphate levels when flow resumed in October 1995. All the characteristics of the spring are consistent with the conclusion that in spite of the proximity of the spring to the pool, it has an entirely separate and unconnected origin.

*Fair Lady Well characteristics in 1995*

On 13 August 1995, Fair Lady Well ceased flowing, leaving a stagnant pool. By 27 September 1995, the water level in the spring was higher, but not yet high enough to overflow into the Ladywell Stream. On 18 October 1995 (more than a month after the pool outflow resumed), the stream was flowing feebly and by 7 November 1995 the stream was flowing strongly. During the time when the stream was not flowing the physical and chemical characteristics in the stagnant pool became highly abnormal. The data from these dates describe a stagnant pool rather than the flowing spring, and were deleted from the data bases used to generate summaries and figures.

By 7 November 1995, the stream was flowing strongly, and all the stream's characteristics were all back to normal. No abnormalities occurred in non-alkaline hardness or sulphate. Because from 13 August 1995 to 18 October 1995 (inclusive) no water was flowing from the spring, the data from these dates describe a stagnant pool rather than the flowing spring. These unrepresentative data were deleted from the data bases used to generate summaries and figures.

## 3.        SULPHATE SURGES IN STREAMS WHICH DRAIN PEAT BOGS

*(a) Sulphate surges in streams*

Although there is no precedent in studies from the Mendip Hills, surges in calcium sulphate concentrations in water draining from fen peat in West Sedgemoor (Somerset) have been described by Heathwaite (1987, 1991). Surges were frequently associated with an increase in discharge following rain. The West Sedgemoor peat was generated in marshes with similarities to those upstream of the Mineries Pool, but on a much larger scale.
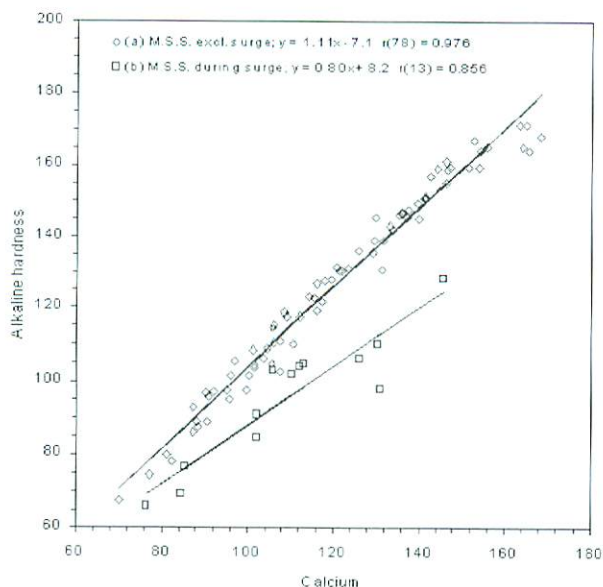
**Figure 8.** *The relationship between alkaline hardness and calcium concentrations (ppm calcite) at St. Cuthbert's Stream, Main Stream Sink (a) before and after the calcium sulphate event and (b) during the calcium sulphate event.*
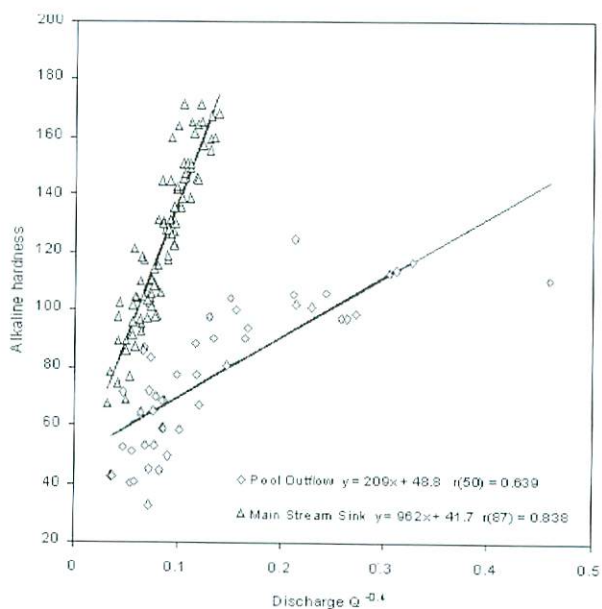


**Figure 9.** *The relationships between alkaline hardness (ppm calcite) and discharge $(Q^{-0.4})$ at the Pool Outflow and the Main Stream Sink.*
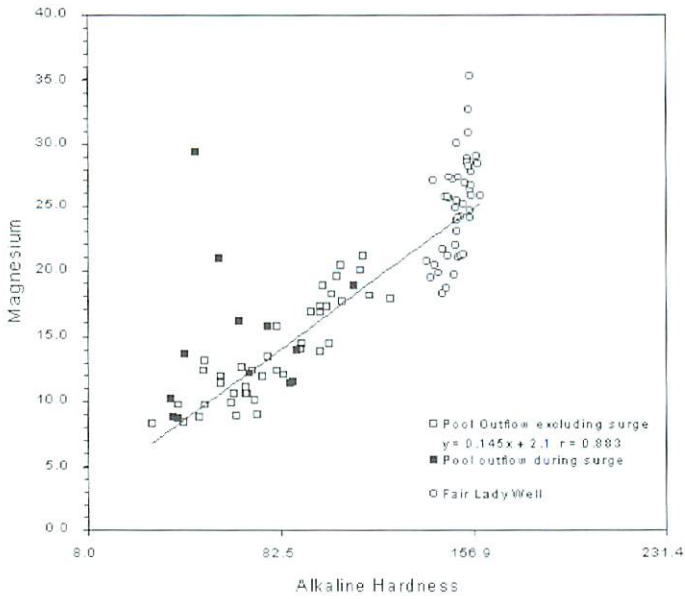
**Figure 10.** *The relationship between magnesium concentrations ($10^5$ x M) and alkaline hardness (ppm calcite) at Mineries Pool Outflow stream and Fair Lady Well.*
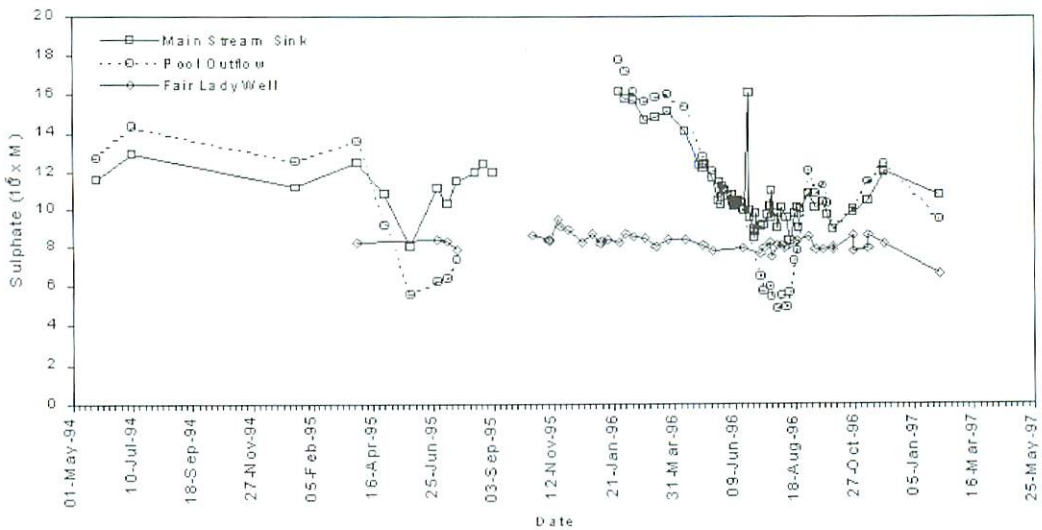


**Figure 11.** *Sulphate concentrations at three stream sites, May 1994 to February 1997, excluding data from the calcium sulphate surge.*

The situation at the Mineries Pool differs from that at West Sedgemoor in an important respect; the solution of calcite in the former site. The present study quantified the relationship between alkaline hardness and discharge in the Pool outflow stream. The calcium sulphate event was found to be a separate, unconnected phenomenon, which had no effect on the alkaline hardness/discharge relationship. However, the alkaline hardness could have had an effect on the calcium sulphate event. As a consequence of the Common Ion Effect, the solubility of calcium sulphate is lower in water containing dissolved calcium hydrogen carbonate than in pure water. High alkaline hardness in water flowing towards the Mineries Pool could therefore have retarded the dissolution of calcium sulphate into that water.

In spite of the differences between marshes at Priddy and those at West Sedgemoor, there are enough features in common to make the results of studies of fen peat relevant to the present study. In West Sedgemoor, sulphate variability at several sites was very high. Concentrations frequently rose sharply to three times those of the low levels found in low-discharge conditions (Heathwaite, 1987, 1991). In the present study, ignoring data from the calcium sulphate event, sulphate concentrations varied between 5 ppm as sulphate at low discharge and more than 15 ppm as sulphate. The similarity between normal (non-event) variations in sulphate in the Mineries Pool outflow stream and those in water draining West Sedgemoor fen peat emphasises the highly unusual nature of the calcium sulphate event at Priddy. Although the variations in the Pool Outflow stream, excluding data from the surge (Figure 11), had a magnitude and range similar to those reported by Heathwaite, the peak of sulphate during the event, nineteen times higher than the base level of sulphate, was of a higher order of magnitude.

*(b) Chemical processes involving sulphur in marshes*

Within West Sedgemoor marshes, sulphur is input in a number of ways; as sulphate dissolved in streams entering the marsh, from gypsum either deposited within peat or in underlying rock or clays, or as hydrated oxides of sulphur in acid rain (Rodhe, 1971). In West Sedgemoor, it was thought that a large proportion of sulphur had been derived from the upper layers of the underlying clays (Heathwaite, 1987). Within the marshes, sulphur may be stored and transformed, and may be discharged from the marshes.

It is known that sulphuric acid may be produced in a peat bog (Gorham, 1958), and the processes which bring about the transformations of sulphur have been described. There are two separate zones of activity within a peat bog. A surface zone where the water is well aerated lies above an anaerobic zone. There is usually a sharp discontinuity separating the two zones, which coincides with a very sharp redox discontinuity.

The anaerobic zone contains significant concentrations of dissolved hydrogen sulphide from the anaerobic decomposition of proteins. In this zone, bacterial reduction of sulphate to sulphide takes place. Sulphur is therefore mobile within this zone. Water discharging from this zone is likely to contain hydrogen sulphide, which will be susceptible to oxidation. In some circumstances (Heathwaite, 1987) the bacterium *Beggiotoa* oxidises hydrogen sulphide to sulphate and elemental sulphur, which may discolour the water (Kuenen, 1975).

Within a peat bog, hydrogen sulphide may enter the aerobic zone, either by a flow of water from the anaerobic zone into the aerobic zone, or by a lowering of the redox discontinuity following a lowering of the water table. In this circumstance, *Thiobacilli* oxidise sulphide to sulphate (Nriagu, 1978). In lime-rich areas, sulphuric acid will be quickly neutralised to calcium sulphate. The solubility of calcium sulphate is low and as temperature rises, the solubility falls.

This can lead to the deposition of gypsum within peat. Horizontal deposits of gypsum were observed in peat in West Sedgemoor, particularly in the upper layers (Heathwaite, 1987).

Experiments carried out to measure the release of nutrients from samples of West Sedgemoor peat following different regimes of prolonged incubation showed that sulphate was particularly mobile (Heathwaite, 1987, 1990).

In Norwegian streams draining an extensive area of bogs, there was a catastrophic fish-kill in the autumn of 1920, after a dry summer. Trout and salmon (adult fish and fry) were killed in large numbers. Investigations showed that the fish were killed by "acid sulphate" (sulphuric acid) produced in the bogs when they dried, and mobilised when rain replaced the water (Huitfield-Kaas, 1922, Dahl, 1923). In the present study there was no acidity, aggressiveness data prove this, although sulphate could have been released initially as sulphuric acid and rapidly neutralised by the abundant carbonate minerals. In the Mineries Pool, populations of fish (rudd, perch, tench and pike) and invertebrates (especially notable dragonfly and damselfly communities) remained healthy during the drought and the following sulphate surge and in the two years following the drought summer.

Laboratory investigations into the release of nitrogen (as $NO_3$ and as $NH_4$), sulphur (as $SO_4$), phosphorus, calcium and magnesium from large samples of drained and undrained fen peat from West Sedgemoor (Somerset) were carried out by Heathwaite (1987, 1990). Duplicate samples were subjected to three long-term regimes: aeration, water-logging and fluctuating aeration and water-logging (all at 20°C). From the results of these studies, she predicted that drainage of currently undrained and waterlogged peat in West Sedgemoor would result in large losses of sulphur, calcium and magnesium to the drainage channels. In particular, she predicted that a pulse of sulphate would be released when flow from the marsh resumed, precisely what had been described and a prediction that Knights and Stenner were astonished to read (Heath-waite, 1987, 1990).

## (c) The frequency of abnormally low water levels in the Mineries Pool

The fact that there was no abnormality in the Mineries Pool Outflow stream after an extremely severe drought in the summer of 1996 is a significant observation. When the authors considered the likelihood of a repeat of the 1995 surge, the fact that there was no surge in 1996 was an important consideration. It was concluded that the surge had been the result of chemical and bio-chemical changes in the waters of the marsh which took place when water levels in the marsh fell considerably. The likely frequency of a water-level fall similar to that in 1995 was considered.

It is not known exactly how long the present regime in the marshes upstream of the Mineries Pool has been in existence. A map which was probably prepared as evidence for a legal dispute which came to court in 1860 shows two large reservoir pools built to supply washing plant near Five Buddles Sink, part of the Chewton Minery. The Mineries Pool did not then exist. The six-inch Ordnance Survey map of 1883 shows the Mineries Pool having replaced the southern dam of the lower reservoir pool of the (by then) derelict Chewton Minery. Between 1883 and 1903, a tramway was constructed to transport material between Chewton Minery and Priddy Minery. This tramway crossed the south-western corner of the Mineries Pool, and an embankment incorporated a siphon to carry excess water from the pool; the Miner-ies Pool Outflow stream. This construction established the current minimum water level in the pool, and in the marshes upstream, which had replaced the former reservoir pools. Water levels in these marshes have therefore been stable for a minimum of 96 years. The water level has not

fallen to the 1995 minimum level at any time since 1953. It is possible that in the years between 1903 and 1953 the water levels in the marshes might have fallen to those seen in August 1995. However, in the severe drought in the summer of 1976, which was reported at the time to have been the most severe drought this century, the water level in the Mineries Pool did not fall to the low level seen in 1995. No samples were known to have been collected for analysis from the Pool or its outflow stream during that summer. The calcium sulphate surge is, therefore, possibly the first such event since the present dam at the Pool was built.

## 4.    A PARTIAL EXPLANATION OF THE CALCIUM SULPHATE SURGE

The precise nature of the mechanisms which caused the event need to be considered further, bearing in mind the highly unusual nature of the event. After the flow from the Mineries Pool ceased in August 1995, the water level in the pool continued to fall for several weeks, in high temperatures, in a drought of unusual severity, to about 1.5 m below the normal low-water level. The marshes upstream of the pool are certain to have drained to an equal extent. It is similarly certain that much of the normally submerged marsh vegetation (including much of the dead vegetation which had accumulated within the marsh) would have dried and decomposed in the unusually hot weather. As the water level in the marsh fell, the level of the redox discontinuity in the water in the marsh is certain to have fallen. Hydrogen sulphide (and iron pyrites) would have been oxidised. It is also likely that calcium sulphate would have been precipitated in the drying marsh as water temperatures rose.

When heavy rain eventually ended the drought, water flowing down the valley towards the Mineries Pool would have flowed through depths in the marsh which were previously inaccessible to the stream. It is here that the sulphate dissolved, either directly as calcium sulphate, or indirectly as sulphuric acid, which was subsequently neutralised to calcium sulphate by contact with limestone. This is the sequence of events that led to the water draining into the Pool becoming almost saturated with calcium sulphate. As this water flowed into the pool, mixing with the water already there, the concentration of calcium sulphate in the pool would have steadily risen. Eventually, the water levels in the marsh upstream of the pool would have returned to normal. The temporary access of water to the lower levels would have been closed as vegetation regenerated. Dissolved salt concentrations and the level of the redox discontinuity in the marsh would have returned to normal. With an inflow of water with normal sulphate levels, concentrations in the Pool (and its outflow stream) gradually returned to normal.

The precise source of the calcium sulphate, however, is uncertain. Oxidation of sulphides in formerly anaerobic layers in the marsh, as parts of the marsh dried out, is certain to have taken place, with a likely contribution by bacteriological activity, involving the release and the oxidation of hydrogen sulphide. There is also the possibility that sulphuric acid could have been produced by the oxidation of iron pyrites. Stanton (*pers. comm.*, 1997) supported this suggestion, because he has frequently observed iron pyrites associated with local samples of galena. For many centuries iron pyrites would have been carried with the lead ore to the Chewton Minery, and discarded there. Iron pyrites previously submerged in the anaerobic zone of the marsh would have been inert. When large parts of the marsh dried out in the exceptional weather conditions in 1995, rapid oxidation of pyrites could have taken place, leading to the production of sulphuric acid, subsequently neutralised to calcium sulphate.

It is also possible that in addition to the processes involving sulphur transformations within the peat (with associated storage of gypsum within the peat), there may have been another origin for sulphur. Subsoil beneath the marsh might contain gypsum, either in clays or in

residues derived from gypsum deposited with the Triassic conglomerate, or from relics of the former cover of Liassic Rocks. When flow restarted after the drought, water would have flowed through this subsoil which is inaccessible to the stream in normal circumstances, thereby dissolving gypsum which contributed to the 1995 event.

There is, therefore, uncertainty concerning the origins of the calcium sulphate, and indeed it is possible that more than one of the three main suggested sources may have been involved. These suggestions should be investigated further. Examination of cores taken from the marshes should make it possible to determine the depths and the stratigraphy of the marshes.

In 1996, although the summer was again unusually dry, the water level in the Mineries Pool did not drop below the level at which the stream outflow ceases. The sequence of events leading to the abnormal solution of calcium sulphate could not have occurred and so there was no repetition of the 1995 calcium sulphate surge.


## CONCLUSION

An unprecedented natural drainage of a normally waterlogged peat marsh on Mendip resulted in a surge of calcium sulphate, together with additional quantities of magnesium sulphate, as previously predicted by Heathwaite. The authors predict that this event will recur, but only following a summer drought so severe that the water level in the Mineries Pool falls substantially below the level at which the overflow ceases.


## ACKNOWLEDGEMENTS

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