

## HYDROCHEMICAL STUDIES IN SWILDON'S HOLE, PRIDDY, SOMERSET

By

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### ABSTRACT

A detailed and comprehensive study was made of the hydrochemical properties of the streams flowing through Swildon's Hole in 1999 and 2000 with additional data being collected in 2002 to permit the inclusion of data from a "normal" dry summer. Measurements were made and water samples were collected in the cave and from the surface streams feeding it. The aim was to measure the concentrations of all ionic species present in the samples in significant levels (accuracy and precision being checked by calculating ion balances). For each sampling trip in the cave it was possible to calculate progressive increments of total hardness and discharge as the stream flowed through the cave. These increments took place as water from the various stream inlets joined the Main Stream. Seasonal changes were assessed in the characteristics of many of the "drip and trickle" inlets. Although many properties showed low variability, data for aggressiveness were particularly instructive. In most inlets beyond Rolling Thunder, pronounced seasonal changes of aggressiveness were found. These changes were consistent with independent observations concerning levels of carbon dioxide in the air in the cave. In addition, all of the inlets beyond Rolling Thunder are contaminated with nitrate, chloride, sodium and potassium, strongly indicating the presence of contamination by human or animal waste. At the six inlets beyond Rolling Thunder as far as Sump I, the presence of faecal bacteria was confirmed. Ion balances were unsatisfactory in most samples that were seriously contaminated by nitrate. Ion balances were satisfactory in the large majority of samples that were not contaminated with large levels of nitrate. Comparisons with earlier data showed that hydrochemical characteristics in the cave have remained stable for 40 years.

### INTRODUCTION

Swildon's Hole is the largest cave in the Mendip Hills, Somerset, in southwest England. Since the discovery of the cave in 1901, many hydrochemical and water tracing studies have been carried out on the cave and its tributary streams. Swildon's Hole is one of the three major swallet caves that flow to the River Axe at Wookey Hole Cave. Its catchment area was estimated by Atkinson (1970) to be 2.9 km<sup>2</sup>. Those of the other two major swallet caves, St. Cuthbert's Swallet and Eastwater Cavern, were estimated to be 1.2 km<sup>2</sup> and 0.7 km<sup>2</sup>, respectively (Smith, 1975, p. 143). Since the catchment area of the cave was calculated, dye testing has proved that the streams from Nine Barrows Swallet and Sludge Pit Hole enter Swildon's Hole (in Passchendaele, off Shatter Chamber; Moody, 1981, 1986, Woodward, *pers. comm.*). This discovery increased the estimate of the catchment area by 0.2 km<sup>2</sup> to 3.1 km<sup>2</sup>.

Figure 1 shows a general map of the area, and the surface topography of the area around Swildon's Hole is shown in Figure 2. Sites within the cave are shown in Figure 3.

*The Priddy pumping station, owned by Bristol Water plc.*

A pumping station owned by Bristol Water plc is situated at N.G.R. ST 52905165, 305 m upstream of the main stream sink. Two surface streams enter the compound enclosing the pumping station. The larger stream overflows from Priddy Pool (at N.G.R. ST 530517), the other (Nine Barrows Hill local drainage stream) drains part of North Hill. The pumping station was built to supply potable water for Street, although later the site became one of many sites

used to gather potable water for Bristol Water plc. There is also a borehole at the site, drilled into water-bearing strata in the Lower Limestone Shales. For many years the pumps were likely to switch into action (and vice versa) without warning. This would cause the size of the stream entering Swildon's Hole to change suddenly and unpredictably, to the alarm of inexperienced visitors to the cave. When the borehole was being pumped, the very great reduction in the discharge of the remaining stream showed that as well as the water from the borehole, pumping removed much of the surface stream from Priddy Pool. This is because the borehole was also designed to act as a temporary reservoir (Newman, 1994). Cattle sometimes graze the land adjacent to the stream between Priddy Pool and the waterworks compound. Therefore water in this stream is intermittently contaminated by cattle waste, causing intermittent contamination of water pumped from the borehole, as noted by Stanton (*pers. comm.*).

Outflow from the waterworks compound surfaces 150 m upstream of the main stream sink, at two pipes shown in Figure 2 as the right pipe and left pipe. The left pipe (facing downstream) carries the residual surface streams (the outflow from Priddy Pool, after water has been diverted into the borehole for storage). It also carries local surface drainage from Nine Barrows Hill, and a variable contribution of overflow water from the borehole). The right pipe (facing downstream) carries water overflowing from the borehole. Since 1994, Bristol Water greatly increased its capacity to draw water from the River Severn and so the Priddy pumping station is now seldom used, except for maintenance work.

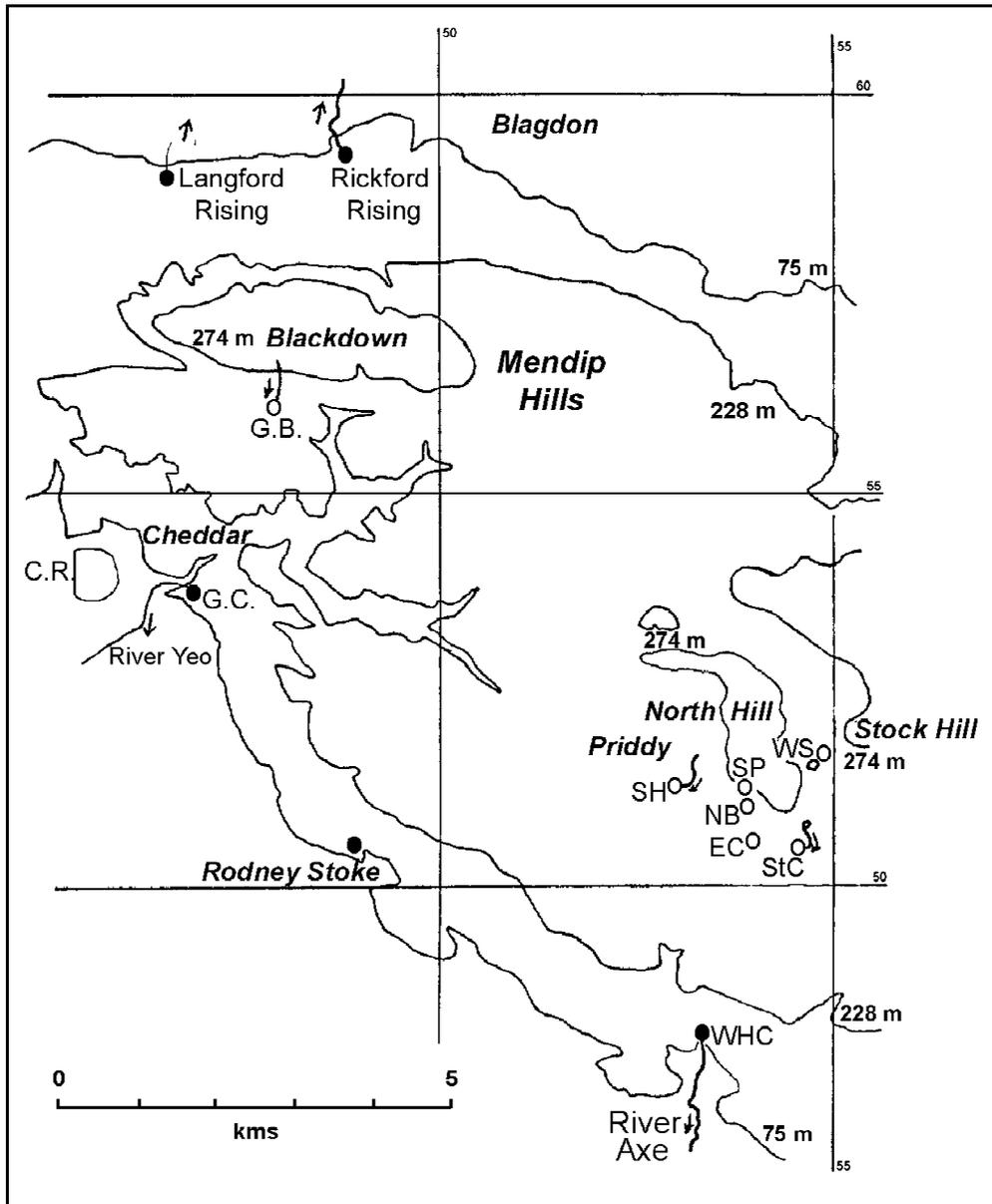
The network of surface streams entering Swildon's Hole becomes larger and more complex as discharge increases (Hanwell and Newson, 1970). In wet weather, part of the outflow from the Bristol Water compound surfaces at two points 100 m upstream of the main discharge points. This water usually sinks again just a few metres upstream of the main exit points (re-emerging mixed with the water in the left pipe). At the main discharge point there is also a third discharge pipe, whose discharge is negligible, of unknown origin.

The discharge of the right pipe (borehole water) is normally smaller than that from the left pipe and the water is usually clear. The left pipe water can become coloured after heavy rain.

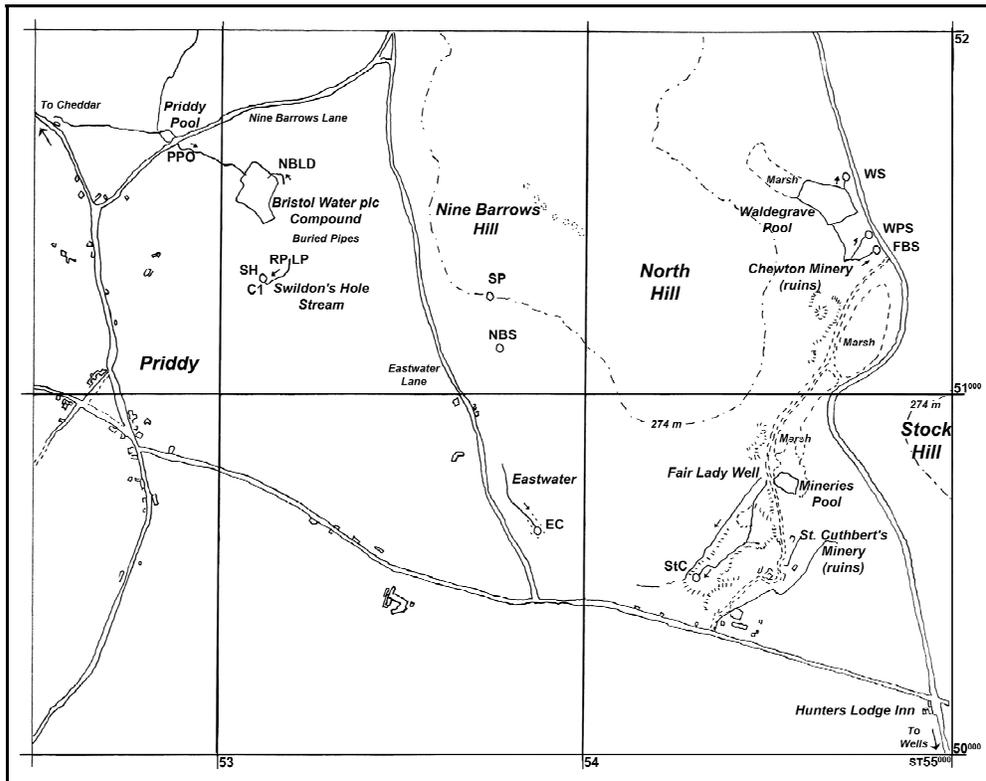
Because the use of the surface streams by Bristol Water plc has changed so much since 1994, there was a high possibility that there might be changes in some of the hydrochemical properties of the stream since that date. There is also a possibility that the local climate (including annual precipitation and temperature) may have changed in the last thirty years, since Atkinson studied the Swildon's Hole surface stream. It was therefore important that a comparison should be made between present hydrochemical characteristics and those reported by Atkinson (1971, 1995), who studied the stream in 1969 and 1970.

The current study was planned in 1998 and the details of sampling and measuring techniques were set out. The cave would be sampled from the surface to Sump 1 in high water, medium water and low water conditions, in summer and in winter. Less regular samples would be collected from the South-east Inlet Series, from the Black Hole Series and from the Stream Passage from Swildon's 4 downstream. The frequency of surface sampling would be considerably higher than that of sampling in the cave to enable a detailed description of the tributary streams to be made.

It was intended that most of the sampling trips would be made in 1999 and 2000 and the first trip took place in February 1999. However, the summer of 1999 was unusually wet and the stream remained unseasonably high throughout the summer. Similarly, the summer in 2000 was also very wet. Consequently the sampling was extended to the summer of 2001 in the hope of obtaining data from normal low water summer conditions. However foot-and-mouth disease



**Figure 1.** General map of the area, showing important streams, stream sinks, springs and associated rivers, and other features mentioned in the text. CR Cheddar Reservoir. Swallets, shown with open circles, are, west to east, G.B. G. B. Cavern, SH Swildon's Hole, SP Sludge Pit Hole, NB Nine Barrows Swallet, EC Eastwater Cavern, StC St. Cuthbert's Swallet, WS Waldegrave Swallet. Major springs, shown with filled circles, are, west to east, GC Gough's Cave, Cheddar, Langford Rising, Rickford Rising, Rodney Stoke spring, WHC Wookey Hole Cavern.



**Figure 2.** Local map of Priddy showing the surface streams entering Swildon's Hole. PPO Priddy Pool Outlet, NBLD Nine Barrows local drainage, RP Right pipe, LP Left pipe SH Swildon's Hole, C1 sampling point at cave entrance, SP Sludge Pit Hole, NBS Nine Barrows Swallet, EC Eastwater Cavern, StC St. Cuthbert's Swallet, WS Waldegrave Swallet, WPS Wheel Pit Swallet, FBS Five Buddles Sink.

intervened, and all access to the cave and to the surface stream was closed. Access was eventually regained and sampling was carried out in the dry spell in late summer 2002. Gut bacteria concentrations in small inlets as far as Sump I were counted successfully. Finally, stream levels started to shrink in the late summer of 2002. Surface sampling took place as water levels fell, and a low-water sampling trip to Sump 1 finally took place, in which the gut bacteria study was repeated. It was not possible to make a hoped-for low water study from Swildon's 4 downstream, but most of the provisional objectives had been achieved.

#### PREVIOUS HYDROCHEMICAL STUDIES IN SWILDON'S HOLE

The present study is the latest of a sequence of studies in the cave. For the first fifty years of the exploration of this cave, when the destination of the stream was uncertain, in particular, there were difficulties with dye tracing experiments as the River Axe, at Wookey

Hole was protected against artificial contamination by a court injunction and the River Yeo at Cheddar used by the Bristol Waterworks Company to fill Cheddar Reservoir (Balch, 1946).

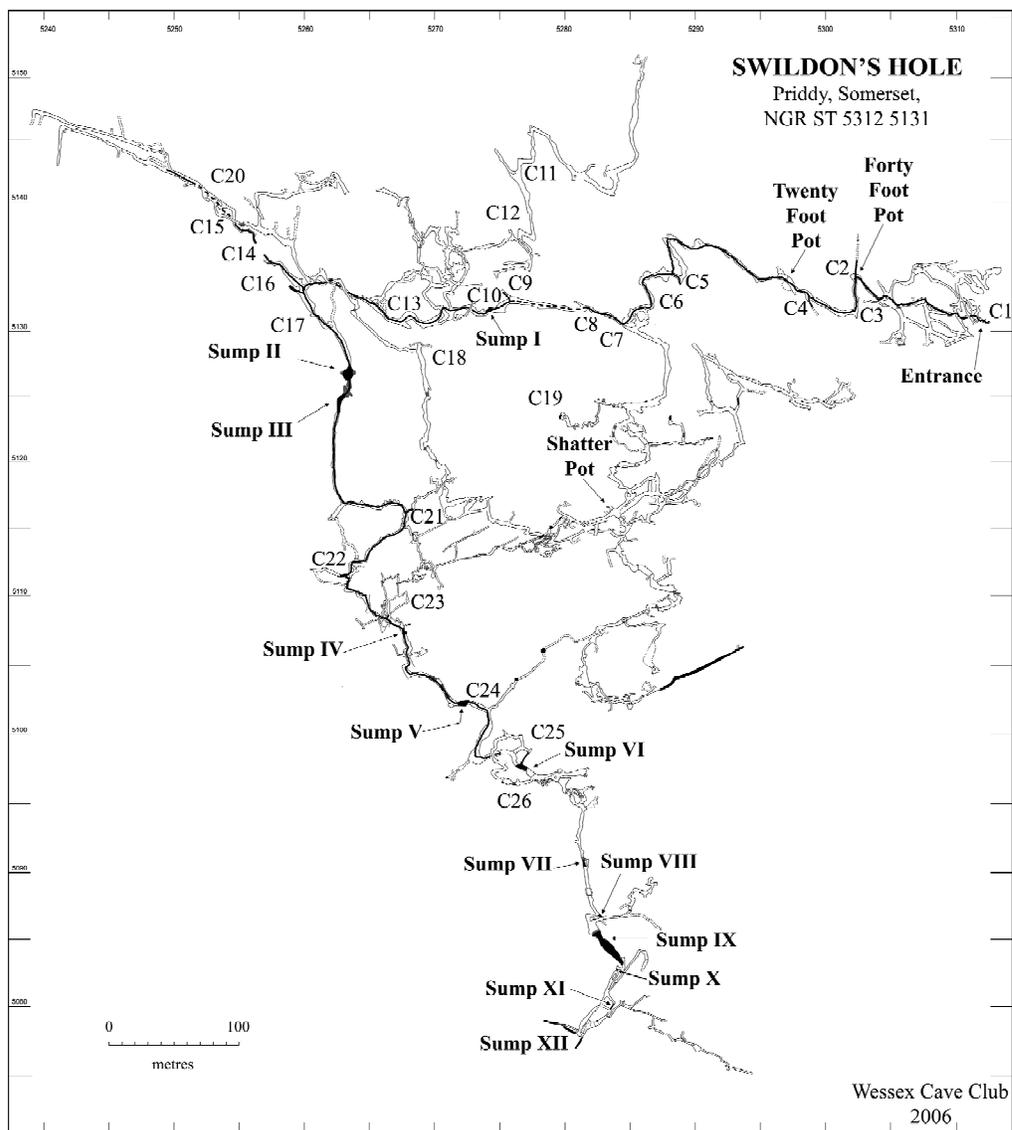


Figure 3. Simplified plan of Swildon's Hole, showing the streams and the sample points.

*Ford*

Dr. Derek Ford analysed water samples from Swildon's Hole for calcium and magnesium, in his study of the geomorphology of the Mendip Hills (Ford, 1963, 1966). He reported the fact that total hardness levels in the surface stream were higher than in St. Cuthbert's Swallet, and much higher than in G.B. Cave. He found very high hardness levels in drip inlet samples from Swildon's Hole. His data were similar to those found by later workers. He discussed the question of increments in calcium carbonate in solution along a stream passage. He questioned the role of addition of calcium carbonate from a very hard water inlet, compared with dissolution of limestone by the stream itself, in causing the increments. He considered the relative sizes of inlet drips and the main stream, and concluded that the drip inlets were too small to increase the hardness of the main stream significantly. However, he noted that at the junction of the Priddy Pool Passage inlet stream with the main stream, the inlet stream was large enough and hard enough to cause the large increase in total hardness usually recorded at this point. Apart from this example, Ford suggested that his data demonstrated progressive increments by solution of limestone as the water flowed through the cave.

*The Mendip Karst Hydrology Project.*

In 1965, the techniques for water tracing using non-polluting dyed *Lycopodium* spores, and fluorimeters for measuring traces of dyes at very low levels became available. The Mendip Karst Hydrology Project was set up in the Geography Department of Bristol University, funded jointly by Bristol Waterworks Co. and Somerset River Board. This study involving staff and postgraduate students of the Geography Department of Bristol University. This has been a key study not only in Swildon's Hole, but for the whole of the Mendip Hills. A program of water tracing experiments and other hydrological research began that were crucial to the understanding of the hydrology of the Mendips (Atkinson *et al.*, 1967). Incorporated in the individual and joint research projects of members of the Mendip Karst Hydrology Project, other workers made important contributions to the understanding of the hydrochemistry of Swildon's Hole.

In 1967, this team, helped by members of all the major Mendip caving clubs, carried out an intensive regional water tracing exercise on Central Mendip. *Lycopodium* spores dyed a number of colours and multiple fluorescing tracing agents were used to try to find connections between the swallets on Central Mendip and the various possible risings (Atkinson *et al.*, 1967). Spores from Plantation Swallet (St. Cuthbert's' Swallet) arrived at Wookey Hole Cave, a straight line distance of 2.86 km, after 11 hours. The first spores from Eastwater Cavern arrived at Wookey Hole Cave, 2.71 km away, after 16 hours, and the first spores from Swildon's Hole arrived there after 25 hours, after traversing 5.46 km. These results ended decades of guessing and speculation about the destination of water entering Swildon's Hole. The time taken for water to flow from a swallet to its resurgence varies considerably depending on the size of the stream, more specifically stream discharge (Stanton and Smart, 1981). It is therefore important to record the fact that the 1967 traces were held in high water conditions. It is clear that Swildon's Hole is one of several swallet cave systems on the Mendip Hills which give variable contributions to the River Axe at Wookey Hole Cave. Their results also suggest that the majority of the cave passages in between are likely to be below the current water table.

*Atkinson.*

In 1969 and 1970, Dr. Tim Atkinson studied the temperature, discharge, total hardness and aggressiveness of the surface stream at approximately weekly intervals for about 10 months. Aggressiveness is the measure of the capacity of water to dissolve or deposit calcite.

He calculated the partial pressure of carbon dioxide (the concentration of carbon dioxide in the soil air) from the aggressiveness and the hardness. He made less frequent measurements of calcium, magnesium, alkalinity and non-alkaline hardness. This research was part of a study of all the major swallet and resurgence caves of Central Mendip (Atkinson, 1971, Smith, 1975). He noted that although the total hardness of the surface stream at Swildon's Hole varied inversely with discharge, the range of hardness values was more restricted than at many other swallets.

*Bridge et al.*

Changes in concentrations of dissolved gases in the short distance from the entrance to the point where the various stream routes recombine at the start of the Wet Way were measured (Bridge *et al.*, 1977). This study included new comparative data from G.B. Cavern and St. Cuthbert's Swallet. The study was important because it answered the question of whether limestone solution in a boulder ruckle is caused by the oxidation of organic matter in solution in the stream, or by gaseous carbon dioxide rapidly passing into solution. It showed that in boulder ruckles, gaseous carbon dioxide passed rapidly into solution and this was followed by the slower solution of limestone. This study also demonstrated that gases passed into solution at the necessary speed.

*Manley and Taylor, and Bacon et al.*

Water samples from the cave were analysed for solutes including sodium and potassium (Manley and Taylor, 1978). Manley and Taylor examined possible patterns in the ratio of the two metals, following suggestions of the possible usefulness of sodium/potassium ratios (Christopher, 1975). Although they found no use for sodium/potassium ratios, they reported enhanced values of both elements in some inlets, suggesting that these inlets were contaminated by human sewage, either raw, or as outflow from a septic tank. They tested the Priddy Pool Inlet for anodic (domestic) detergents, and the result was positive, indicating pollution by domestic sewage. This study supported the earlier discovery of high levels of gut bacteria (*Escherichia coli*) in the Priddy Pool Passage inlet, close to Sump 1 (Bacon *et al.*, 1963).

## LIMESTONE SOLUTION

Picknett's study of the solution of calcite in the water/calcite/carbon dioxide system at 10°C (Picknett, 1964) showed that there are 7 equilibria involving the various ionic and molecular species in the system. The concentration of carbon dioxide in solution at 10°C will depend on that of carbon dioxide in the air that is in contact with the water. Starting with carbon dioxide-free water and bring it into contact with ordinary air, carbon dioxide will pass from the air into the water until the two levels are in equilibrium. At this stage the concentrations will be stable. This does not mean that nothing is happening. Carbon dioxide will be passing from the air into the water at exactly the same rate that carbon dioxide will be passing back from the water into the air. The rates of movement from air to water, and from water back into the air are usually slow, but the more unbalanced the concentrations are, the faster will be the transfer rates. Rates of movement from water to air and from air to water will increase considerably if there is a greater area of surface contact, or if there is greater turbulence. In carbon dioxide-free water, a small amount of limestone solution will take place. In the presence of dissolved carbon dioxide, dissolved carbonate ions will react to become hydrogen carbonate ions, and more calcite will dissolve to re-establish the equilibrium between calcium and

carbonate ions. Given a large source of carbon dioxide-laden air, carbon dioxide will continue to pass into the water and more calcite will dissolve until the 7 reactions are once more in equilibrium.

The net result is a relationship between the dissolved calcium and the carbon dioxide in solution with the carbon dioxide in the air. The concentration of calcium (and hydrogen carbonate) in solution will increase very rapidly as the concentration of carbon dioxide rises. The level of calcium in equilibrium with normal atmospheric air (with 0.03% carbon dioxide, by volume) is only approximately 70 mg/l (ppm) at 10°C. However in soil air, much higher levels of carbon dioxide are present. Given soil air with a concentration of 10% carbon dioxide by volume, the corresponding equilibrium concentration of calcium will rise to approximately 500 mg/l (ppm) at 10°C.

Various factors can influence the size of the various components in equilibrium. Importantly, if the water temperature rises, the solubility of carbon dioxide in water falls. Carbon dioxide will de-gas into the air, and the dissolved calcium concentration will fall.

When water that has reached equilibrium with the surrounding air emerges into a cave, a study of the physical chemistry of the water will provide information about the conditions through which the water has recently flowed. If the water emerges at a constant temperature, and with stable (constant) calcium hydrogen carbonate levels, then the water has flowed through a zone where it has been in equilibrium with a constant concentration of air carbon dioxide. If the cave air contains a lower level of carbon dioxide than that behind the drip, then carbon dioxide will begin to slowly degas into the cave air, upsetting the equilibria, making the water supersaturated and capable of depositing calcite. Conversely, if the cave air has a higher carbon dioxide level, then carbon dioxide will begin to pass into the water, giving it the capacity to dissolve more calcite. There will be a change in the aggressiveness towards calcite (a quantitative measure of the capacity of water to dissolve or deposit calcite). The chemical characteristics of inlet water samples reveal information details about the passages through which the inlet has flowed before reaching the sample site, and of the changes that have taken place since the water entered the cave atmosphere

#### *The relationship between total hardness and stream discharge.*

Ford (1966, *ibid*) stated the possibility that there might be an inverse relationship between the hardness of a stream and the discharge of the stream. This possible relationship was investigated by Atkinson at a number of swallets and resurgencies on Mendip in 1969 and 1970. The Swildon's Hole stream was one of the sites he studied, and the Nine Barrows Swallet stream, which enters Swildon's Hole in Passchendaele in the Shatter Series, is another. He found an inverse relationship between the total hardness and discharge at most sites. Since Atkinson studied the Swildon's Hole stream, the usage of water from the stream has changed considerably, and because of this change it was important to compare the present characteristics of the stream with those recorded by Atkinson. It was also considered important to compare the relationship with those established in studies at St. Cuthbert's Swallet. Here, statistically significant relationships were found between total and alkaline hardness with a discharge function ( $Q^{-0.4}$ ) (Heathwaite *et al.*, 1999). However, hardness changes were sometimes out of phase with changes of discharge (Knights and Stenner, 2001).

## THE PRESENT STUDY

The aim of the present study was to make the most complete study of the major solute constituents in the streams of Swildon's Hole carried out to date.

### *Sampling sites.*

The major inlets between the Entrance and Sump I would be sampled in high, moderate and low water conditions, in summer and in winter. The sites selected were close to the Main Stream and included relatively small inlets, such as the two near Tratman's Temple, in addition to the largest inlet in the cave, the misnamed Priddy Pool Passage inlet. Selected sites between Sump 1 and Sump 3 would be sampled less frequently. These inlets included those in the Black Hole Series, North-west Stream Passage (including some smaller inlets), and the inlet in Caliper Pot. This inlet was included because when a pollution incident took place in the cave (Sparrow, 1993) after diesel fuel was dumped in Priddy, it entered the cave via Caliper Pot. Inlets from Swildon's IV to Swildon's IX would be sampled infrequently by cave divers. These sample sites included the drip inlet at Cowsh Aven, and the stream from Nine Barrows Swallet which enters the cave via Passchendaele. The sites are shown in Figures 2 and 3. In addition to collecting the major water samples from the inlets, data from upstream and downstream of the sites where the inlets joined the main stream, temperature, discharge when possible and small water samples were also collected. These subsidiary samples were taken to enable stream discharge ratios to be calculated by the Method of Mixtures.

### ***Field and Laboratory Methods***

#### *Water Sampling*

Samples were collected and stored in clean 500 ml wide mouth HDPE bottles. After use, the bottles were rinsed with 20% hydrochloric acid and three rinses of tap water, then three rinses of double-distilled water and drained dry. At the sample site, the bottles were triple rinsed with the water being sampled, and wherever possible, filled by completely immersing the bottle, and closed tightly with the triple rinsed lid under water, excluding all air bubbles. Care was taken not to include any sand, gravel or mud, because recent studies have shown that including either calcareous gravel or clay-like deposits can lead to serious errors (Knights and Stenner, 1999). If the water could not be sampled without including solid material, the water was filtered through a fluted Whatman no. 541 paper. Site details and water temperature were permanently recorded on the card sheet for the trip, including the numbers of any samples that had been filtered. At sites where it was not possible to fill a bottle completely, as much water as possible was collected.

Water temperatures were measured with an electronic thermometer with a resolution of 0.1°C, checked before use with a mercury-in glass thermometer read to a resolution of 0.02°C.

At every stream junction, the Method of Mixtures was used to calculate the discharge ratio between the discharge of the inlet stream and that of the main stream. Water samples were taken from the inlet stream and the main stream upstream of the junction, and from the main stream downstream of the junction. Thorough mixing was ensured by choosing the downstream sampling site downstream of a feature (such as a stretch with very turbulent flow) that ensured that the two streams had thoroughly and evenly mixed together.



Flow rate of the potassium chloride solution: d l/min

For further details of measuring stream discharge by salt dilution, see Stenner and Stenner, 2001.

The salt dilution measurements were made when the collecting teams were nearing the surface, and collecting the samples (from the cave and from the surface sites) had been completed. The bottles containing standard potassium solutions and the salt dilution gear was kept strictly separate from the rest of the sampling equipment. This ensured that there was no possibility of contaminating samples with potassium. There is no scheme for preparing and circulating "round robin" samples in Karst studies in Britain. As in other recent studies involving R.D. Stenner, the quality of the analytical work was demonstrated by analysing most samples for all ions present, and calculating the ion balance in the samples. In a sample in which every analysis was satisfactory, the ion balance error would equal the standard error for the complete determination (calculated below).

*The order of analysing the samples.*

The samples were first checked to ensure that all the bottle numbers were clear, all the expected samples were present, no unexpected problems had occurred during the trip and all information was transferred to a standardised (paper) work sheet. A spreadsheet file was prepared for the sampling trip. The order in which the analyses were carried out was justified by recent studies that demonstrated the stability of various quantities (Knights and Stenner, 1999). In that work, it was shown by repeated analyses that in samples stored in the dark in cool conditions, concentrations of  $Mg^{2+}$ ,  $Na^+$ ,  $K^+$ ,  $Cl^-$ ,  $SO_4^{2-}$  and  $NO_3^-$  did not change. Concentrations of  $Ca^{2+}$ , alkaline and total hardness and aggressiveness were stable only for relatively short times, when stored in completely full sample bottles in optimum conditions. These critical quantities were all analysed as quickly as possible, and the sample bottles were then stored until it was possible to complete the remaining stable quantities.

The analyses for total and alkaline hardness and aggressiveness to calcite were carried out within 24 hours of collection. Two twin-tap micro-burettes (10 ml  $\times$  0.01 ml) were set up. The burette with a bottle of 0.02 M EDTA solution was (after thorough mixing) thoroughly rinsed with the EDTA solution. The beakers, Grade A 10.0 ml pipettes and flasks to be used were thoroughly washed, finally with three rinses of double-distilled water. The fresh bottle of standard AnalaR magnesium iodate was then used to standardise the EDTA solution. Three titrations were carried out and if the results were self-consistent, the standardisation of the EDTA was complete. If needed, further titrations were made. Standard hydrochloric acid (recently made up from a Volucon vial) was used (with Grade A pipette and Grade A volumetric flask) to make up a fresh batch of 0.02 M hydrochloric acid. This batch of standard acid would only be used for the one day. This acid was used to rinse and fill the second burette.

The densities of the samples in all the sample bottles were equalised by inverting three times. The samples were then analysed, in the order of the sheet, for total hardness. The total hardness titrations were all repeated. On the rare occasions when a mistake was made, a third titration was needed. All the burette readings, including any mistakes, were recorded on the sheets, and the mean value of the titrant was calculated and recorded on the sheet. Next the sample saturated by calcite was titrated. This sample was mixed four times by inversion, so by now the excess calcite would have settled leaving the supernatant solution clear. The clear solution could now be pipetted without disturbing the calcite residue, and titrated with the standard EDTA solution. The first sample was then titrated with the standard acid in the second burette for alkaline hardness, using two drops of BDH 4.5 mixed indicator. The titration was

continued until the colourless stage was stable for a full four minutes. Some of the titrations were repeated to check that the method was proceeding correctly, but for many samples the single titration result was accepted without being repeated. The titrations were continued (lit when needed with a daylight bulb) until the total hardness, alkaline hardness and aggressiveness measurements of all the samples had been completed. At this stage the measurements were entered into the spreadsheet set up for the trip. On every occasion these titrations were completed within twenty four hours of collection. A third similar burette was then set up and filled with 0.02 M silver nitrate solution, and 20 ml aliquots of the samples were titrated for chloride using the Mohr titration. An indicator blank is needed for this titration. The silver nitrate solution is stable for many weeks, and although chloride concentrations in natural water are stable, it was convenient to complete all the volumetric analyses in a single session. The sample bottles were packed and stored in a dark cool area until they could be analysed in the Environmental Chemistry laboratory at Bristol University.

At this stage, the results so far were perused. From the data, the non-alkaline hardness was determined by subtracting the alkaline hardness from the total hardness.

At Bristol University, the next (second) set of determinations was carried out using a Cambridge 917 spectrophotometer burning propane and compressed air from cylinders. Working standard solutions were made up freshly for magnesium, sodium and potassium. With the spectrometer in the atomic absorption (AA) mode the set of samples was analysed for magnesium, and in the flame emission (FES) mode, the samples were analysed for sodium and potassium. The results were entered into the same working sheet, for later transferring into the same spreadsheet file.

At this stage, the stream discharge at the surface was calculated. Then, using data from around every stream junction or drip inlet site, the stream discharge ratios at every stream junction were calculated, hence the discharge of the inlet. In some cases the inlet was too small to cause a change in the properties of the main stream. Even in these cases it was often possible to calculate the maximum inlet size consistent with this result.

On the spreadsheet file, the calcium concentration was determined by subtracting the magnesium concentration from the total hardness.

The third set of analyses was to determine nitrate and sulphate levels. Nitrate levels were determined using an Orion 720 a meter with a nitrate ion selective electrode (I.S.E.) by EIL, using the inbuilt program for determining concentrations by I.S.E. The sulphate levels determination were found by a turbimetric method using a standard barium chloride solution and an EEL laboratory spectrometer. When these determinations were complete, the spreadsheet was completed, and ion balances calculated.

Some samples were analysed for ammonium ion concentrations, using Nessler's reagent. To 10 ml of the sample, 1 ml Nessler's reagent was added. The same volume of the reagent was added to the same volume of standard solutions containing known concentrations of nitrogen in ppm nitrogen as ammonium. The intensity of red coloration is proportional to the concentration of ammonium ions present. However, in every sample analysed, the coloration was paler than that in the first standard solution, so the next stage of the analysis (determining the intensity of the coloration in the samples and in the standards with a colorimeter) was abandoned. All the samples were recorded as having less than 1 ppm (1 mg/l) nitrogen as ammonium ( $7.143 \times 10^{-5}$  M ammonium). In three batches of samples, 15 (from 20 samples), 3 (from 14 samples) and 11 (from 11 samples) were analysed for ammonium and the result "<1 mg/l" was recorded.

*Determining the concentration of presumptive Coliform bacteria*

These determinations were carried out twice, in 23<sup>rd</sup> December 2001 and 5<sup>th</sup> September 2002. Ready-prepared 10 cm diameter Petri dishes, each containing 10 ml MacConkey Agar gel, were purchased from Oxoid Ltd. A roll of Sellotape was needed, and a graduated 2 ml medical syringe (without a needle) was needed to inoculate each plate with freshly sampled water *at the sampling site*. Two plates were labelled before the trip for each site to be sampled, and two blank plates were retained on each trip. Taking care not to breathe over, or drip water over the freshly uncovered dish, the well rinsed syringe was used to place 2 ml of the water being sampled on the surface of gel. The gel was covered, and the sample was spread over the surface of the gel by rotating briskly for five seconds in one direction, then for five seconds in the opposite direction. The cover was briefly lifted to drain off any excess water, and the inverted dish was then securely sealed with Sellotape. The second plate was then inoculated in the same way, and the plates were then stored for the rest of the trip.

The inoculated and the blank plates were collected immediately on reaching the surface, and placed in a battery-operated incubator. The plates were incubated at 38°C, and inspected at 24 hours and thereafter every 12 hours until the colonies had developed to a sufficient size for reliable counting. No attempt was made to estimate concentrations of *Salmonella* bacteria, and no re-culturing was undertaken to allow speciation of the bacteria to be attempted. The number of red-coloured colonies were counted, and reported as presumptive *Coliform* bacteria. In each trip, the blank dishes gave zero counts. Using this procedure it was possible for ordinary cavers to make useful bacteriological measurements, safely, without using specialised trained bacteriologists.

Copies of the data tables have been deposited with UBSS, and are available on request.

*Accuracy and precision*

For each of the characteristics analysed, the following standard errors were calculated (as  $10^5 \times \text{Molar}$ ,  $\sim \text{ppm CaCO}_3$ ):

Total hardness, calcium and aggressiveness to  $\text{CaCO}_3$ , 1.6;  
 alkaline hardness 6.0;  
 non-alkaline hardness, 7.6;  
 magnesium, 0.46;  
 sodium, 3.0;  
 potassium, 1.2;  
 chloride, 2.6;  
 sulphate, 3.1;  
 nitrate, 4.7.

Many of these values are higher than those quoted in the St. Cuthbert's Swallet study. The total standard error of the ion balance (univalent) was calculated as follows:

$$\begin{aligned} \text{Overall standard error} &= \text{SE} = (\text{SE}_1^2 + \text{SE}_2^2 + \text{SE}_3^2 + \dots)^{1/2} \\ &= (3.2^2 + 3.0^2 + 1.2^2 + 12.0^2 + 6.2^2 + 2.6^2 + 4.7^2)^{1/2} \\ &= 15.3 \times 10^{-5} \text{ M (univalent)}. \end{aligned}$$

### ***Investigating ion balances***

#### *Total cations.*

The total cation concentration (monovalent) =  $2 \times \text{total hardness} + 1 \times \text{sodium} + 1 \times \text{potassium} + 1 \times \text{ammonium}$  (Units Molar, univalent).

#### *Total anions.*

The total anion concentration (monovalent) =  $2 \times \text{alkaline hardness} + 1 \times \text{chloride} + 2 \times \text{sulphate} + 1 \times \text{nitrate}$  (Units Molar, univalent).

#### *Ion balance error (IBE).*

Ion balance = total cation concentration – total anion concentration (Units Molar, univalent).

Theoretically, the ion balance will be zero where all the constituents have been measured perfectly correctly. The IBE therefore serves to measure the overall reliability of the experimental work, and to demonstrate that all the ionic constituents in the sample have been determined. The standard error of each measured constituent determined was calculated from the present analytical data. Considering the concentrations used to calculate IBEs, the total standard error has been shown to be  $15.3 \times 10^{-5}$  M (univalent). This value is close to the observed IBEs in the present study in samples with “normal” nitrate levels.

### ***Scrutiny of the data***

On completion of the field work the data was scrutinised to identify data that had been affected by clearly identifiable mistakes. With such a large number of participants, this is a serious source of potential error. Cross plots between various pairs of constituents were made to distinguish individual as opposed to systematic outliers. Possibly anomalous data were noted and marked for further investigation. Several anomalous data-points were then shown to have a single cause, which had resulted in both an anomalous data point on an inter-species regression graph and an unsatisfactory ion balance for the sample concerned. For example, water samples collected on 19<sup>th</sup> October 2000 were analysed for sodium and magnesium on the same day with the same spectrophotometer. Sodium/chloride and magnesium/calcium regressions were examined. In the main stream at the cave entrance, sodium and magnesium results were seriously low, and the sodium level was substantially lower than the chloride level, which was normal. Values for magnesium (and calcium) and sodium at the site for the date were deleted from the database. It is thought that on the day these samples were analysed for sodium and magnesium there was an intermittent partial blockage of the instrument’s aspirator tube, resulting in the errors observed. On the other hand, at the same date, sodium levels in the right pipe stream were also low. However, concentrations of chloride in this stream were also very low. Because of this satisfactory sodium/chloride balance, the sodium and chloride values for this sample trip were accepted.

The following nine bad data-points were also identified. At the left pipe stream on 29<sup>th</sup> April 2000, the Priddy Pool outflow stream on 1<sup>st</sup> October 2000, and the Nine Barrows Hill local drainage stream on 26<sup>th</sup> March 2000, 31<sup>st</sup> May 2000 and 19<sup>th</sup> October 2000, non-alkaline hardness values were very low compared with sulphate concentrations (where there is usually an approximately 1:1 relationship). It was judged that the alkaline hardness titrations had been inaccurate, and alkaline hardness and non-alkaline hardness values for these data-points were deleted from the data-base. Finally, at the left pipe stream on 10<sup>th</sup> March 2000 and 31<sup>st</sup> May

2000, the right pipe stream on 22<sup>nd</sup> November 1999 and the Priddy Pool outflow stream on 29<sup>th</sup> December 1999, values for sulphate were unusually low and showed a large discrepancy when compared with values for the non-alkaline hardness. The sulphate values for these data-points were judged to be inaccurate and were deleted from the database.

When the inaccurate data-points were deleted from the database, the standard deviations for magnesium, sodium, non-alkaline hardness and sulphate, generally, did not improve. In fact, in some cases they worsened. This result contrasts with that in a similar exercise with St. Cuthbert's Swallet data (Knights and Stenner, 1999), when the standard deviations always became smaller after unreliable figures were deleted. This contrast will be commented on below.

## RESULTS:

### 1. THE SURFACE STREAMS

Summaries of the hydrochemical properties of four surface stream sites associated with the Swildon's Hole main stream at the cave entrance are shown in Table 1. The properties of the two outflow pipes from the Bristol Water compound, which combine to form the main stream at the cave entrance are shown in this table. Also shown in Table 1 are the two distinct surface streams that enter the Bristol Water compound (the outflow from Priddy Pool and a small stream draining part of Nine Barrows Hill). Nine Barrows Hill local drainage stream drains an area where cattle grazed intermittently. The properties of the Nine Barrows Hill surface drainage stream showed widely variable concentrations of nitrate, chloride, sodium and potassium (consistent with intermittent contamination with waste from cattle grazing at the site). Compared with other nearby swallet streams, levels of total hardness, calcium and alkaline hardness were relatively high at all five stream sites. The mean values of each of these properties were slightly higher at the right pipe (looking downstream) than at the other four surface site. More significantly, the standard deviation of each of these properties (and that of the aggressiveness at this site) was lower in the right pipe stream than at the other four surface sites.

Time series graphs of the Swildon's Hole main stream at the cave entrance in the present study are shown in Figure 4A. Figure 4C presents similar graphs plotted from data from Atkinson's study of 1969 and 1970 (Atkinson, 1995). Figure 4B shows the relationship between the total hardness and the discharge function ( $Q^{-0.4}$ ) in the present study, and Figure 4D shows the same relationship plotted from Atkinson's study (Atkinson, 1995).

Figure 5 shows the major characteristics of five sites connected with the Swildon's Hole main stream, from the outflow from Priddy Pool to the cave entrance. It was not possible to include error bars in the diagrams that make up Figure 5. The standard errors are shown in the caption of each part of Figure 5.

The results presented in Figure 5 show that many of the constituents components (notably total and alkaline hardness, calcium) were consistently higher in the right pipe water than in the other four surface sites. Apart from water temperature and discharge, there was no sign of seasonality in trends.

The results in the graphs for total hardness, magnesium, calcium and alkaline hardness in Figure 5 show the following feature. The graphs from the Priddy Pool outflow stream, the left pipe water and the Main Stream at the cave entrance were very similar in general shape, and lower in magnitude than the relatively invariable right pipe water. This pattern can be seen most clearly on the three instances when the values fell to very pronounced lows; on 30<sup>th</sup>

	Disch l/min	Temp. °C	Tot. Hard	Agg.	Mg	Ca	Alk. Hard	Non- AlkH	Cl	NO <sub>3</sub>	SO <sub>4</sub>	Na	K	An's	Cat's	Imbal
<b>Surface Stream, at cave entrance (C1)</b>																
No.	24	22	23	21	20	20	21	21	21	20	20	21	21	20	20	20
Mean	1577	11.0	184.7	-1.7	21.1	164.1	170.1	13.6	21.1	26.8	10.5	25.0	4.3	395	407	-12.7
StdDev	2298	1.81	17.4	3.86	4.86	14.5	16.0	2.69	2.88	10.7	3.00	3.24	0.79	37	38	13.4
RSD	146	16.5	9.4	-231	20.8	8.8	9.4	19.8	13.7	39.8	28.5	13.0	18.2	9	9	-106
Min	0	6.8	149.5	-8.6	11.2	131.8	137.0	7.9	16.0	10.3	5.4	11.8	1.7	326	319	-49.4
Max	12000	14.7	205.8	9.3	30.1	182.4	188.0	18.4	27.2	54.0	14.8	27.5	6.2	443	452	10.4
<b>Left Pipe (looking downstream) contribution</b>																
No.	24	22	23	22	20	20	23	21	21	19	18	21	21	18	18	18
Mean	1160	12.0	180.8	-0.4	20.4	160.3	168.4	12.7	20.7	25.0	10.0	25.6	4.3	383	395	-11.6
StdDev	1955	2.11	20.1	2.56	4.55	17.0	18.6	4.08	3.35	11.4	4.02	1.74	0.70	42	46	13.7
RSD	169	17.6	11.1	-655	22.3	10.6	11.1	32.1	16.2	45.5	40.1	6.8	16.4	11	12	-118
Min	0	6.4	136.9	-7.6	12.8	121.7	125.0	-0.9	15.2	6.9	0.0	19.8	3.1	303	293	-33.8
Max	10010	15.6	205.8	3.9	30.1	182.4	188.0	18.4	27.2	50.2	16.5	27.6	6.3	443	452	12.3
<b>Right Pipe (looking downstream) contribution</b>																
No.	24	18	19	18	16	16	19	17	17	15	15	17	17	15	15	15
Mean	341	12.0	196.4	-0.7	23.1	173.5	182.4	14.6	21.9	32.2	8.9	24.9	4.4	422	434	-11.5
StdDev	448	2.53	5.44	1.36	3.09	5.82	5.19	2.63	5.47	11.7	3.29	2.93	0.64	13	18	16.4
RSD	132	21.0	2.77	-185	13.4	3.35	2.84	18.0	25.0	36.3	36.9	11.8	14.3	3	4	-142
Min	0	9.3	187.4	-2.9	14.7	165.4	174.0	9.0	16.0	17.0	0.0	13.5	2.3	404	407	-43.8
Max	2025	15.8	207.3	1.4	27.9	184.4	190.0	18.8	41.6	58.3	14.5	27.4	5.2	446	461	15.2
<b>Stream draining part of Nine Barrows Stream</b>																
No.	23	14	15	14	14	15	15	15	15	13	11	15	15	11	11	11
Mean	4	14.1	199.6		31.6	174.3	171.4	28.2	42.0	39.5	12.8	49.1	13.2	425	417	8.5
StdDev	6	5.42	69.3		18.9	51.8	46.0	27.0	22.4	30.8	8.5	32.7	5.9	160	122	63.0
RSD	161	38.3	34.7		59.6	29.7	26.8	95.9	53.3	78.0	66.1	66.5	44.6	38	29	743
Min	0	2.8	111.3		11.9	112.4	105.0	-3.4	15.2	8.7	5.3	18.3	6.0	262	271	-120.5
Max	26	26.2	313.1		64.4	253.3	253.5	85.1	91.2	118.9	33.0	153.6	25.5	757	657	145.0
<b>Priddy Pool Outflow Stream</b>																
No.	16	18	16	15	15	18	17	17	17	15	13	17	17	13	13	13
Mean	13.9	170.8	-0.9	19.0	151.3	161.5	9.5	17.8	18.4	9.5	24.6	2.8	368	375	-6.8	
StdDev	4.71	26.2	5.54	5.51	24.7	26.2	4.79	3.28	12.5	4.75	4.07	1.30	56	60	18.6	
RSD	33.9	15.4	-603	29.0	16.3	16.2	50.5	18.5	67.8	49.8	16.5	46.2	15	16	-275	
Min	3.1	104.1	-10.9	11.4	92.7	96.0	-2.3	12.8	3.2	0.0	10.1	0.8	236	255	-43.6	
Max	22.1	210.7	14.3	28.0	183.4	203.0	20.9	26.4	41.2	17.5	28.8	5.9	445	478	20.0	

**Table 1.** Characteristics of surface streams entering Swildon's Hole February 1999 to September 2002. Concentrations  $10^5 \times$  Molar, discharge  $l\ min^{-1}$ . Ion balances univalent.

September 1999, 26<sup>th</sup> March 2000 and 19<sup>th</sup> August 2000. On these three occasions, the common pattern was that the Priddy Pool outflow water had the lowest values, the left pipe values were slightly higher, then the main stream sink water, with the relatively invariable right pipe water highest. There was a fourth low value on 26<sup>th</sup> November. On this occasion the pattern was not seen as clearly as at the other three instances, because there were no immediate subsequent results when the characteristics of the streams returned to normal values.

The trend for non-alkaline hardness in the five streams sites in Figure 5 was similar to that in the other hardness-related constituents, but the pattern was not so strictly adhered to. Among the other constituents, there were sometimes shared similarities (such as shared peaks and troughs) in chloride, nitrate, sodium and potassium, but these shared patterns were not as pronounced as those seen in the main hardness characteristics. In the aggressiveness to calcite (Figure 5G), the absence of seasonal pattern (or indeed of any other type of pattern) was noted.

The Nine Barrows Swallet stream is a tributary to the Swildon's Hole system, joining the Main Stream in Swildon's 6. Although the Nine Barrows Swallet stream was not monitored in the present study, relevant data by Atkinson is presented here. Figure 6A is a time series showing the relationship between total hardness and discharge at Nine Barrows Swallet. The relationship between the size of the stream at Nine Barrows Swallet and that of Swildon's Hole surface stream in 1969 and 1970 is shown in Figure 6B. A statistical summary of data from Atkinson's 1969-1970 study of Nine Barrow's Swallet is shown in Table 2.

	Q l/sec	Temp	Total Hard.	Ca	Mg Hard.	Alk.	Non- AlkH	Agg.	pH	spH	pCO2
Swildon's Hole stream, Atkinson (Nov. 1969 - Sep. 1970).											
No	30	5	30	16	16	5	5	28	7	7	28
Mean	8.41	6.32	185.7	160.1	16.9	139.4	21.2	-2.71	7.71	7.67	0.87
S.D.	9.98	1.32	30.58	22.38	5.2	54.26	6.49	8.14	0.16	0.19	0.29
R.S.D.	118.7	20.9	16.5	14	30.7	38.9	30.6	-300	2.13	2.49	33.4
Max	44.4	8.1	229	183	29.5	208	31.6	10	8	8	1.57
Min	0.03	4.6	95	105	10	76	14	-26	7.55	7.4	0.25
Nine Barrows Swallet stream, Atkinson (Nov. 1969 - Sep. 1970).											
No	5	20	20	14	14	3	3	20	7	7	19
Mean	4.56	0.61	66.45	56.14	11.11	35.6	25.73	6.22	7.94	8.35	0.2
S.D.	1.71	0.73	15.97	14.95	1.96	3.17	7.18	5.39	0.23	0.31	0.13
R.S.D.	37.4	120.6	24	26.6	17.7	8.92	27.9	86.7	2.93	3.74	62.1
Max	7	3.3	107.5	93	15	38	32.2	19	8.3	8.7	0.49
Min	2.4	0.1	49	40	8.5	32	18	-2.5	7.65	8	0.03

**Table 2.** Characteristics of two surface sites at Swildon's Hole, Nov. 1969 to Sep. 1970, Data from Atkinson (1971).

#### *A comparison of present data from the surface streams with those from earlier studies*

Ford presented very limited data for the chemical characteristics of the surface stream; just the mean (181 ppm as calcite) and the range (164-194ppm as calcite) of the total hardness of at least five samples. The range was similar to that found in the present study. Ford's units are numerically indistinguishable from those used in the present study. Ford's study is discussed in more detail below. The data from the main stream at the cave entrance in the present study were compared with those from Atkinson (1995) made in his study in 1969-1970. The total hardness and discharge data from the two studies are shown in Figure 4., and these and other measurements are shown in Tables 1 and 2. Atkinson reported a wider range of total hardness data than is found in the present study. His maximum and minimum values for total hardness were 229 and  $95 \times 10^{-5}$  M respectively compared with 205.8 and  $149.5 \times 10^{-5}$  M respectively in the present study. Nevertheless, when Atkinson's summaries (not only total hardness and discharge, but calcium, magnesium, alkaline and non-alkaline hardness, aggressiveness to calcite) were compared with those in the present study, differences were not significant (at the P=95% level). The absence of significant differences between these two

comparable data sets obtained with similar methods at the same location over 30 years is noted. Both studies show that the total hardness at the site is higher than at neighbouring sites and both studies show the total hardness at the site varies considerably less than is usual. The very important relationship between total hardness and discharge will be discussed separately, below. When Atkinson was making his study of the stream, the water was frequently pumped from the borehole, a practise that had ceased during the present study. It is suggested that the difference in the total hardness range and differences in the response of hardness to discharge were the result of the change in the use of the stream by the waterworks company.

### ***The relationship between total hardness and discharge.***

The relationship between total hardness and discharge at the cave entrance is shown as a time series in Figures 4A and 4C. The relationship between the two properties is shown in the scatter plots in Figures 4B and 4D. Atkinson observed that the range of total hardness values at the site was narrower than usual. The range in the present data was even narrower than in Atkinson's data, and the contrast with other nearby sites is considerable. This visual contrast is echoed in the fact that the regression equations of the graphs between total hardness and discharge function are considerably lower than those found at St. Cuthbert's Swallet and G.B. Cave. The pattern in Atkinson's data is closer to the normal pattern than that in the present study, with a more pronounced response of total hardness to changes of discharge.

It is reported that, on several occasions, the data were unexpected (using experience of stream studies at G.B. Cave and St. Cuthbert's Swallet). The total hardness data, in particular, sometimes seemed to unexpectedly high or low, considering the discharge at the time. It is claimed that anomalous data points are curious, but nevertheless, the present data are correct. It is believed that some data points were anomalous because the samples were not collected at the optimum stages in a hydrological cycle. For example, data from 18<sup>th</sup> November 2000 are seriously anomalous. The discharge was by a huge margin the highest recorded in the recent studies and much higher than any recorded by Atkinson, but the total hardness was relatively high, nowhere near the lowest recorded, as might be expected. The magnitude of the discharge was such that the station normally used for making discharge measurements could not be used. There were no grounds for doubting the reliability of the measurements. Flattening of bank-side grass showed that the discharge had been considerably greater shortly before the stream was sampled on 18<sup>th</sup> November 2000. When the discharge was at its peak, it is likely that the hardness would have been considerably lower and that after this optimum time, the rise in hardness had been faster than fall in discharge. This is a suggestion that could be tested by further studies in the future

A similar anomaly between discharge and hardness was found by Bray in his studies of Ogof Ffynnon Ddu (South Wales) in 1974 (Bray, 1975 and *pers. comm.*).

There were similar occasions in the St. Cuthbert's Swallet study when total hardness was "out of phase" with the discharge (Knights and Stenner, 2001). The precise sequence of changes of total hardness and discharge following a rainstorm needs to be investigated in detail, but this can only be achieved by using remote sampling and monitoring equipment. Such an approach has been used in a study of cold water mineralization in an Australian cave (James, 1975), and in a stream tracing exercise in the Peak District (Christopher *et al*, 1981).

In severe floods, the size of the surface stream reaches values far greater than that recorded on 18<sup>th</sup> November 2000. During floods on 24<sup>th</sup> November 1954 (Kenney, 1955), on 17<sup>th</sup> January 1959, (Frost, 1959) and on 10<sup>th</sup> July 1968 (Irwin, 1968), the discharges must have been much, much greater.

***The absence of seasonal variations in hydro-chemical properties.***

The data from each of the five surface sites was divided into separate sub-sets for summer (May to September inclusive) and winter (November to March inclusive). The results were examined for any evidence of a seasonal influence on any hydro-chemical properties. The differences of water temperature and discharge were significant, which had obviously been expected. However, no other differences were significant at the  $P = 95\%$  levels. The total, alkaline, non-alkaline hardness, aggressiveness to calcite, calcium, magnesium, sodium, potassium, chloride, nitrate and sulphate showed no seasonal influence. Differences between summer and winter data were outstandingly small in water leaving the Bristol Water compound via the right pipe. In the Nine Barrows Hill local drainage stream, there were apparently large non-seasonal fluctuations in the mean total and alkaline hardness, chloride, nitrate, sodium and potassium. However, because the variabilities of many of the characteristics in this little stream are very high, possibly a consequence of varying cattle grazing activities in the neighbourhood, the differences were not statistically significant.

***The flow of water through the Bristol Water plc compound near Swildon's Hole.***

The streams entering the pumping station 305 m upstream of the cave entrance are now piped and buried, together with the outflow water from the borehole drilled into water-bearing strata at the site. The outflow stream from Priddy Pool (N.G.R. ST 52855170) is the largest discrete stream entering the waterworks compound. The small intermittent stream draining a south-western segment of Nine Barrows Hill also enters the compound.

From the pumping station compound, water is piped to the main overflow point 152 m upstream of the main stream sink. Overflow from the Priddy borehole reaches the surface in the right pipe (looking downstream) and the left pipe carries surface streams. In wet weather, part of the outflow from the Bristol Water compound surfaces at two points 100 m upstream of the main discharge point. The overflow water usually sinks again just a few metres upstream of the main exit points. When this water was deliberately stirred up, the muddy water re-emerging mixed with the left pipe water. At the main discharge point there is also a third discharge pipe, whose discharge is negligible.

Although left pipe water can be coloured after heavy rain, right pipe water was clear and colourless on every occasion in the sampling period. The characteristics of the tributary water sources will be examined in much greater detail below.

***Swildon's Hole streams compared with nearby streams.***

The three major swallet caves in Priddy, Eastwater Cavern, St. Cuthbert's Swallet and Swildon's Hole, are shown in Figures 1 and 2. These caves engulf streams draining North Hill, Priddy. The largest stream enters Swildon's Hole, the most westerly of the three caves. To the east is Eastwater Cavern, which takes the smallest stream, with the shortest route on the surface. The most easterly cave, St. Cuthbert's Swallet, takes two separate distinct streams, the outflow stream from the Mineries Pool and a stream draining part of Stock Hill (St. Cuthbert's Stream). It also takes (intermittently) some of the outflow from a spring, Fair Lady Well. In addition to these major streams, and the associated major cave systems, there are several minor streams draining North Hill, and some small caves. Two very small streams draining a part of North Hill enter two small swallet caves between Eastwater Cavern and Swildon's Hole, Nine Barrow's Swallet and Sludge Pit Hole. Both of these streams have been proved to enter

Swildon's Hole in Passchendaele, a passage in the Shatter Series. In addition, there are three small intermittent streams associated with Waldegrave Pool, on the eastern flank of North Hill (Waldegrave Swallet, Wheel Pit Swallet and Five Buddles Sink. The remnant of Ladywell stream, emerging from beneath the western wall of the Belfry, now sinks in a recently discovered cave, Rose Cottage Sink. No studies have yet been made of most of these tiny streams. Details of the various separate streams draining North Hill are shown in Table 3.

No data are available from the tiny stream at Sludge Pit, or from the intermittent streams sinking at Wheel Pit Swallet or Five Buddles Sink. However, the very limited study of samples from Stock Hill Mine suggests that water sinking at the two last-named sinks is very similar in chemical make-up to that sinking in Waldegrave Swallet.

The mean total hardness in the constituents of Swildon's Hole main stream (left pipe water, the outflow from Priddy Pool and the borehole component) were all higher than at the other nearby cave streams. The total hardness of the streams at St. Cuthbert's Swallet were intermediate in magnitude. However, in the streams connected with that cave system there was a clear division between data from the Fair Lady Well water and St. Cuthbert's stream on one hand, and those from the Mineries Pool outflow stream on the other. The total hardness of the surface stream at Eastwater Cavern was the lowest of the three largest streams, while the most easterly stream draining North Hill, Waldegrave Swallet stream, had the lowest mean total hardness. The stream entering Nine Barrows Swallet was somewhat harder than Eastwater Cavern stream, but the stream was much smaller than any other stream listed in the table.

A comparison of the variabilities of each stream showed important differences. The total hardness of Fair Lady Well, a natural spring at the Old Red Sandstone/Lower Limestone Shale junction, was high, and outstandingly stable. Other characteristics of this stream (temperature, alkaline hardness, magnesium, chloride, nitrate, sulphate, sodium and potassium), were also extremely stable (Knights and Stenner, 2001). It is important to note that this site was sampled at the resurgence, the well itself. On the other side of St. Cuthbert's valley, the characteristics of St. Cuthbert's stream were also notably stable. As at Fair Lady Well, much of the flow here was also subsurface. The total hardness of the water overflowing from the Mineries Pool was much more variable, as were other characteristics of the stream, such as magnesium, sulphate, alkaline and non-alkaline hardness. The total hardness of Eastwater Cavern stream was variable, and similar in this respect to the Mineries Pool outflow stream, but total hardness values in Eastwater Cavern stream were lower. No detailed information of the other components in the stream is known. Similarly, no detailed information about the Nine Barrows Swallet stream is known. At Swildon's Hole, the total hardness of Priddy Pool outflow stream the surface drainage stream (the left pipe stream) and the borehole water (the right pipe stream), showed low variability. The total hardness of the borehole water had the least variability, and the other constituents also had a very low variability. Results in Tables 1 and 3 show that the variabilities of total, alkaline and non-alkaline hardness, calcium and magnesium were lower in the right pipe water than in other sites connected with Swildon's Hole. However, when compared with water from Fair Lady Well, only total and alkaline hardness and calcium had the same outstandingly low variability. The discharge of the right pipe stream was also slower to fall after a period of heavy rain, compared with the left pipe discharge. The similarity to the characteristics of water from Fair Lady Well was pronounced. It is possible that the similar (but less pronounced) stability of the Priddy Pool outflow stream is a sign that this stream has an

Stream	Q l/min	No.	S.D.	Tot Hard $10^{-5} \times M$	No.	S.D.	R.S.D. %	Min $10^{-5} \times M$	Max $10^{-5} \times M$
Priddy Pool outflow stream 1999-2002	19.3	24	32.6	170.8	18	26.2	15.4	104.1	210.7
Right pipe stream (from borehole) 1999-2002	6.81	20	7.70	196.4	19	5.44	2.77	187.4	207.3
Stream draining part of 9 B. Hill, 1999-2002	N.D.			199.6	15	69.3	34.7	111.3	313.1
Swildon's Hole, Entrance, 1999-2002	26.3	24	38.3	184.7	23	17.4	9.4	149.5	205.8
Nine Barrows Swallet stream, 1969-1970	0.60	20	0.73	66.4	20	16.0	24.0	49.0	107.5
Eastwater Cavern stream, 1969-1970	2.3	24	5.1	55.3	24	11.2	20.2	37.5	79.0
Fair Lady Well stream, 1994-1997	N.D.			160.8	46	5.08	3.16	149.1	168.5
Mineries Pool outflow stream, 1994-1997	9.65	60	14.0	94.4	60	20.6	22.1	50.5	135.8
St. Cuthbert's stream by str. ratios, 1994-1997	8.70	45	10.2	169	45	26.2			
St. Cuthbert's stream, cave ent. 1994-1997	13.2	91	14.0	135.2	97	26.8	19.8	80.7	185.0
Waldegrave Swallet stream, 1969-1970	3.9	15	3.52	25.3	15	7.1	28.2	12.5	37.5

**Table 3.** Characteristics of streams entering swallet caves draining North Hill, Priddy. No details are available for the very small intermittent stream entering Sludge Pit Hole. Details of Swildon's Hole streams are from the present study, those for St. Cuthbert's Swallet are from Knights and Stenner, 2001, details for Nine Barrows Swallet stream, Eastwater Cavern and Waldegrave Swallet stream are from Atkinson (1995).

important contribution from springs in the Lower Limestone Shales through which it flows (several springs are shown on the map of the area). The Priddy Pool outflow stream is the major contributor to the left pipe stream, although the left pipe stream receives a variable contribution from the borehole outflow.

At the cave entrance, the combined stream was usually slightly supersaturated, with little variability. The aggressiveness at the surface had no seasonal trend.

### ***Comparisons between the various surface streams.***

When characteristics such as total hardness at two different sites along a stream are measured, the question arises as to whether the differences are caused by changes such as limestone solution within the same discrete stream, or are caused by admixture with water from a different stream. In previous studies, this question has been tested in this way; if samples from two different stations in a stream consistently show significant differences in non-alkaline hardness (or other stable solutes such as chloride or sulphate), then it may be inferred that water from a different stream has been mixed with the principal stream.

This test was applied to data from this study. Between the Priddy Pool outflow stream and the Nine Barrows local drainage stream, there were frequently considerable differences of non-alkaline hardness, chloride, nitrate, potassium and magnesium. These differences are typical of those found in two separate unconnected streams with different origins.

The Priddy Pool outflow stream was then compared with the left pipe stream from the Bristol Water compound. The Priddy Pool stream enters the Bristol Water compound, and from the compound emerge the left pipe and the right pipe (downstream) streams. Figure 5(b) shows that the pattern of variations of total hardness in the left pipe stream is very similar to that in the Priddy Pool outflow stream, and quite unlike the right pipe stream. Exactly the same pattern was seen in Figure 5(d) (for calcium) and Figure 5(e) (for alkaline hardness). Differences in non-alkaline hardness were relatively small. Most concentrations of chloride, nitrate, sodium and magnesium were very similar, but most of the potassium concentrations in the left pipe stream were higher than in the Priddy Pool Outflow Stream. These results show that the left pipe stream is derived from the Priddy Pool Outflow Stream with negligible additions. The water had dissolved a variable concentration of calcium hydrogen carbonate plus a smaller concentration of magnesium hydrogen carbonate, from the solution of limestone, together with an increase in dissolved potassium. The left pipe stream was derived mainly from the Priddy Pool outflow stream. Chemical changes caused by additions from the tiny Nine Barrows local drainage stream were negligible. At this stage it is not possible to say whether the measured components between the Priddy Pool and the left pipe stream were the result of chemical changes within the surface stream, or the consequence of addition of water from the bore-hole.

Similar calculations were made of changes between the Pool Outflow Stream and the right pipe stream and gave very similar results to those between the Pool Outflow Stream and the left pipe stream. This result was a surprise. The chief difference was that in each case one sample in each case showed a big rise of chloride or nitrate. The conclusion is that in spite of the outstanding stability of important characteristics in the right pipe water, the water in this stream was fundamentally derived from the Priddy Pool outflow stream. The stream then acquired its special characteristics during the time of its storage in the well, by reactions with limestone and supernatant air within the well. Water finally emerges as the right pipe stream with its special characteristics, such as stable high concentrations of total, calcium and alkaline hardness. These conclusions are consistent with observations by Stanton, and amplify his observations (Stanton, *pers. comm.*).

The fact that the main stream at the entrance shows patterns similar to those in the left pipe stream is to be expected from the discovery concerning the origin of the right and left pipe streams.

Figures 5(b), 5(d) and 5(e) show features that are strikingly similar to those seen in the St. Cuthbert's Swallet study (Knights and Stenner, 2001, Figure 8 and Figure 4). Although the right pipe stream clearly shows its basic origin in the Priddy Pool outflow stream, comparisons of alkaline hardness in the St. Cuthbert's Swallet study shows conclusively that Ladywell Stream is completely unconnected with the Mineries Pool Outflow stream. While total, calcium and alkaline hardness characteristics have great similarities, this characteristic is not shared by other components. This is because the hardness components share a common origin (the  $\text{CaCO}_3/\text{CO}_2/\text{H}_2\text{O}$  system), and this is not true of other components. Variations in chloride (Figure 5(h)) and sodium (Figure 5(k)) are completely different. They do not vary in an apparently systematic pattern, possibly sodium and chloride might vary depending on storm events. A much higher sampling frequency would be needed to establish such a relationship.

#### ***Nitrates in surface streams.***

Atkinson did not determine concentrations of nitrates in the water. In the Tynning's Swallet stream, in the River Axe at Wookey Hole Cave and in the River Yeo at Cheddar, a large increase in nitrate concentrations between 1968 and 1969 has been reported (Chapman *et al.*, 1999). Data concerning nitrate levels in several Mendip resurgences obtained by Bristol Water plc from 1935 to 2000 have been published recently (Jones and Smart, 2005). The method of analysis used by Bristol Water chemists varied. In the earlier years, they reduced nitrates to ammonia, which was determined using Nessler's reagent, the intensity of the red coloration being determined using comparator tubes. The Bristol Water results were presented as mg nitrogen/litre. The results were recalculated to the units used in the present study ( $10^5 \times$  Molar nitrate ions). The results for the Cheddar Spring show an increase in nitrate levels from  $6 \times 10^{-5}$  M in 1935 to  $42.8 \times 10^{-5}$  M in 1997, the majority of the increase having taken place since 1970. Stenner recorded nitrate values from the Cheddar spring in 1996 and 1997 with a mean value of  $39.3 \times 10^{-5}$  M, and from 2000 the values ranged from  $59.3$  to  $64.9 \times 10^{-5}$  M. Similarly, Stenner's limited data for nitrate concentrations in the Langford and Rickford springs in 1998 were extremely close to those reported by Jones and Smart. No old data for nitrate levels in the Swildon's Hole surface stream is available.

#### ***Surface samples that gave unsatisfactory ion balances.***

It was explained above how 9 measurements from surface stream site samples were judged to be unsatisfactory, and were deleted from the database. When a similar exercise had been carried out on data from the St. Cuthbert's Swallet Study, the exercise had affected the statistical summary of the results. The mean and the standard deviations of the IBEs decreased, showing that the mistakes that had been identified had adversely distorted the statistical summaries (Knights and Stenner, 1999). Identifying the errors had contributed significantly to improving the precision of that study. In the present study, however, although the deletion of the nine unsatisfactory measurements had improved the standard deviations and the RSDs of the quantities involved, there were no corresponding improvements in the standard deviations and RSDs of the IBEs. This conclusion was a disappointment and a surprise. It suggests that in the present study, errors in the practical (laboratory) work were not the main source of poor IBEs. This realisation prompted a new approach to the analysis of IBEs in the present study.

	Disch. (l/min)	Temp. (°C)	Tot. Hard	Agg.	Mg	Ca	Alk. Hard.	Non. Alk H.	Cl	NO3	SO4	Na	K	Ion Bal	Imbal
<b>Surface (C1)</b>															
No.	24	22.0	23	21	19	19	21	21	21	20	20	20.0	21	19	19
Mean	1577	11.0	184.7	-1.7	21.6	163.5	170.1	13.6	21.1	26.8	10.5	25.7	4.32	-10.7	-1.3
StdDev	2298	1.81	17.40	3.86	3.86	14.65	16.00	2.65	2.88	10.67	3.00	1.36	0.79	10.66	1.47
RSD	146	16.50	9.42	-230.8	17.86	8.96	9.41	19.39	13.68	39.79	28.48	5.29	18.22	-99.4	-109.8
Min	0	6.8	149.5	-8.6	14.0	131.8	137.0	7.9	16.0	10.3	5.4	22.4	1.69	-37.7	-5.3
Max	12000	14.7	205.8	9.3	30.1	182.4	188.0	18.4	27.2	54.0	14.8	27.5	6.20	10.4	1.6
<b>Water Chamber upstream of Old Grotto stream</b>															
No.	1	3	4			1									
Mean	480.5	8.93	181.83		23.4	183.9									
StdDev		2.09	20.99												
RSD		23.45	11.54												
Min		6.1	151.6												
Max		11.1	207.3												
<b>Old Grotto stream</b>															
No.		4	4		2	2									
Mean		9.9	184.0		20.20	162.4									
StdDev		1.89	23.13		3.20	27.75									
RSD		19.17	12.57		15.84	17.09									
Min		6.7	151.6		17.0	134.6									
Max		11.7	213.5		23.4	190.1									
<b>Water Chamber downstream of Old Grotto stream</b>															
No.	3	7	7		2	2									
Mean	1706	9.87	189.6		24.60	181.2									
StdDev	883.6	1.42	18.90		0.90	5.95									
RSD	51.8	14.36	9.97		3.66	3.28									
Min	480.5	7.0	150.2		23.7	175.2									
Max	2530	11.4	210.8		25.5	187.1									
<b>Rolling Thunder Inlet (C2)</b>															
No.	5	6	6	6	6	6	6	6	6	6	6	6.0	6	6	6
Mean	219.9	11.1	208.0	1.7	20.5	187.5	188.5	19.5	26.0	24.3	13.7	29.4	4.16	-5.1	-0.537
StdDev	162.5	2.9	5.86	14.28	1.65	6.49	3.07	3.82	4.61	10.58	3.44	2.09	0.32	12.55	1.342
RSD	73.9	26.4	2.82	856.6	8.05	3.46	1.63	19.58	17.74	43.52	25.07	7.11	7.69	-245.4	-250
Min	34.5	8.1	199.4	-17.6	17.7	177.9	183.5	13.5	18.4	12.5	8.7	26.4	3.60	-27.3	-2.847
Max	458	15.9	215.7	23.8	22.4	196.3	193.0	24.1	31.2	44.5	18.8	32.6	4.63	8.5	0.919
<b>Heavy Drip downstream of Rolling Thunder (C3)</b>															
No.	6	5	6	6	6	6	5	5	5	6	6	6.0	6	5	5
Mean	5.5	12.4	283.7	-12.8	21.4	262.3	217.7	56.5	18.4	140.1	9.1	18.3	2.42	-38.9	-3.3
StdDev	6.23	3.12	28.78	9.83	3.24	26.63	25.14	7.87	3.32	27.14	4.18	1.55	0.51	30.90	2.57
RSD	112.7	25.22	10.14	-77.03	15.11	10.15	11.55	13.93	18.03	19.37	46.07	8.46	20.90	-79.41	-78.51
Min	0.0	9.7	249.8	-27.8	17.0	229.4	193.5	49.9	12.0	98.8	2.3	15.7	1.74	-86.1	-7.0
Max	14.3	16.7	331.3	0.0	25.1	307.2	263.0	71.5	20.8	169.8	14.0	20.1	3.19	3.4	0.3
<b>Drip Inlet above 20' Pot (C4)</b>															
No.	5	6	6	6	6	6	6	6	6	6	6	6	6	6	6
Mean	142.4	10.7	263.7	-9.5	14.1	249.5	229.1	34.6	15.2	73.4	7.0	14.5	1.99	-16.9	-1.5
StdDev	134.1	1.72	23.46	9.12	3.16	20.73	27.78	6.13	3.10	15.07	2.41	0.82	0.39	14.85	1.32
RSD	94.1	16.07	8.90	-96.16	22.39	8.31	12.13	17.72	20.38	20.52	34.60	5.69	19.54	-87.66	-90.4
Min	38.0	9.5	232.6	-24.1	10.0	221.6	195.0	23.9	8.8	49.7	4.6	13.4	1.58	-36.5	-3.2
Max	402.0	14.4	296.7	0.9	17.6	279.6	264.0	44.5	18.4	98.4	11.9	15.7	2.56	8.5	0.8
<b>Drip Inlet at Barnes' Loop (C5)</b>															
No.	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
Mean	11.7	11.3	318.7	-9.2	25.4	293.3	247.9	70.8	26.9	136.2	15.6	26.9	2.90	-23.0	-1.6
StdDev	4.74	2.89	6.96	13.26	2.78	6.95	6.34	5.46	3.32	42.32	3.67	1.14	0.38	40.96	2.85
RSD	40.48	25.56	2.18	-143.9	10.94	2.37	2.56	7.72	12.33	31.08	23.52	4.26	13.15	-178.2	-179.40
Min	2.9	9.6	310.3	-32.4	21.9	284.2	235.0	63.3	20.8	75.3	8.7	24.9	2.54	-100.8	-6.8
Max	16.5	17.7	326.5	5.8	29.6	303.4	255.0	76.9	31.2	216.3	20.3	28.7	3.51	31.8	2.4
<b>Inlet in Trat's (C6)</b>															
No.	6	6	6	6	6	6	5	5	6	6	6	6	6	5	5
Mean	9.6	12.5	305.3	-11.4	15.8	283.8	244.0	57.7	26.9	114.2	13.7	32.3	5.25	-5.7	-0.2
StdDev	15.45	3.14	16.09	15.17	2.26	10.21	17.69	13.22	6.07	55.41	3.51	5.67	1.60	50.56	4.04
RSD	160.4	25.19	5.27	-133.1	14.28	3.60	7.25	22.90	22.53	48.52	25.69	17.55	30.43	-886.9	-1980.0
Min	0.0	9.6	278.1	-33.5	13.4	264.7	223.5	38.7	17.6	12.3	8.6	24.6	2.53	-60.2	-4.3
Max	42.0	17.8	323.3	5.8	19.3	298.9	277.0	80.0	34.4	185.7	19.5	41.4	7.69	86.0	7.3
<b>Inlet below Trat's, Inlet (C7)</b>															
No.	5	4	5	5	5	5	5	5	5	5	5	5	5	5	6
Mean	7.5	11.7	310.5	-8.5	16.6	293.9	250.3	60.2	24.2	134.8	13.7	25.0	4.37	-36.4	-2.1
StdDev	12.78	2.51	25.28	8.13	2.72	24.86	20.16	7.32	5.87	31.68	1.82	8.15	1.38	27.89	2.27
RSD	170.4	21.47	8.14	-95.61	16.34	8.46	8.05	12.15	24.28	23.50	13.34	32.57	31.64	-76.63	-107.44
Min	0.0	9.9	277.1	-20.8	12.4	261.5	224.0	53.1	17.6	93.1	10.4	14.5	2.87	-85.3	-6.4
Max	33.0	16.0	350.3	2.3	20.8	333.1	276.5	73.8	32.0	175.8	15.0	32.7	6.50	-7.8	0.7

	Disch. (l/min)	Temp. (°C)	Tot. Hard	Agg.	Mg	Ca	Alk. Hard.	Non. Alk H.	Cl	NO3	SO4	Na	K	Ion Bal	Imbal
<b>Main Stream upstream of Priddy Pool Passage (C8)</b>															
No.	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
Mean	1771	10.7	197.6	5.2	21.8	175.9	182.3	15.4	22.5	20.6	10.2	26.6	4.37	-1.7	-0.1
StdDev	660	1.43	12.01	16.31	2.86	10.26	10.90	3.09	2.67	8.40	4.14	0.96	0.50	11.8	1.4
RSD	37.3	13.43	6.08	312.7	13.12	5.83	5.98	20.09	11.85	40.82	40.53	3.60	11.48	-675.8	-1157.0
Min	510	9.4	183.4	-16.7	17.3	162.4	169.0	10.5	19.2	9.3	2.0	25.5	3.80	-16.6	-1.9
Max	2568	13.8	217.4	31.3	26.3	194.6	198.0	19.4	26.4	30.0	14.5	28.1	5.20	17.9	2.3
<b>Priddy Pool Passage Inlet Stream (C9)</b>															
No.	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
Mean	174.2	11.6	340.6	-8.5	21.6	319.0	296.8	43.8	31.5	97.1	16.0	34.0	11.12	-27.9	-1.84
StdDev	62.54	3.06	5.93	10.10	2.51	5.28	6.90	3.77	2.34	25.11	4.95	2.17	1.55	27.59	1.77
RSD	35.91	26.42	1.74	-119.3	11.62	1.66	2.32	8.62	7.44	25.86	30.99	6.39	13.97	-98.79	-96.58
Min	65.0	9.7	331.9	-24.1	17.8	310.0	287.5	37.5	27.2	67.2	10.0	30.5	8.90	-83.9	-5.42
Max	252.0	18.4	348.1	8.8	24.8	325.5	307.0	49.6	34.4	147.0	23.5	36.3	13.80	-1.0	-0.07
<b>Main Stream Sump 1 (C10)</b>															
No.	6	6	6	6	6	6	6	6	6	6	5	6	6	5	5
Mean	1978.8	10.78	210.8	4.1	21.9	188.9	191.9	18.9	22.8	27.3	12.8	27.3	4.95	-6.3	-0.63
StdDev	725.9	1.52	13.35	15.92	2.85	11.62	11.49	2.10	2.60	9.16	3.79	0.86	0.57	12.95	1.40
RSD	36.7	14.10	6.33	391.4	13.01	6.15	5.99	11.08	11.41	33.52	29.61	3.17	11.53	-206.0	-222.2
Min	575.0	9.5	193.6	-14.3	17.5	172.6	177.0	16.1	19.2	16.7	7.4	26.4	4.36	-27.7	-2.89
Max	2766.0	14.1	232.1	33.3	26.2	208.8	210.0	22.1	25.6	42.8	17.6	28.8	6.01	8.3	1.00
<b>Well Chamber, Black Hole (C11)</b>															
No.	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mean	10.1			-36.5	17.6	-17.6				70.7	14.2	22.7	3.47		
<b>Passage to Black Hole, Inlet (C12)</b>															
No.	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mean	93	10.5	283.1	-16.2	17.9	265.2	235.0	48.1	26.4	202.9	19.4	22.3	10.9	-138.8	-10.375
<b>Main Stream downstream of Creep 1 (C13)</b>															
No.	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Mean	2781	10.1	218.0	10.8	21.4	196.7	197.3	20.8	25.6	35.2	18.0	27.8	5.27	-22.2	-2.13
<b>Downstream of Wet Ears Squeeze (Northwest Stream Passage) (C14)</b>															
No.	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Mean	10.6	344.5	-1.4	21.5	323.1	303.0	41.5	46.4	63.3	21.5	58.9	17.4	6.71	0.41	
<b>Upstream of Wet Ears Squeeze (Vicarage Passage) (C15)</b>															
No.	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Mean	9	10.4	431.0	-30.5	28.6	402.4	340.5	90.5	120.8	170.7	24.1	70.8	23.9	-64.1	-3.08
<b>Muddy Sump Inlet (C16)</b>															
No.	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mean	93	9.9	343.2	-57.4	32.6	310.6	261.0	82.2	112.0	311.1	52.2	190.2	55.6	-117.3	-5.919
<b>Main Stream downstream of Muddy Sump (C17)</b>															
No.	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Mean	1689	9.95	222.8	13.10	21.60	201.2	202.5	20.32	27.20	28.05	12.55	28.45	5.89	-5.38	-0.58
<b>Caliper Pot (C18)</b>															
No.	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mean	10.1	308.0	-8.3	31.9	276.1	257.5	50.5	32.0	92.7	16.0	33.1	9.20	-13.3	-1.000	
<b>First Mud Sump (C19)</b>															
No.	1	1	2	2	2	2	1	1	1	2	1	1	1	1	1
Mean	6	12.0	294.7	-15.9	15.4	279.3	222.5	38.8	118.4	152.1	17.2	240.0	1.39	-33.5	-2.148
<b>Northwest Stream above Pitch (C20)</b>															
No.	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mean	292.8			-8.8	14.3	278.5	273.0	19.8	28.8	76.5	20.0	30.2	3.97	-71.6	-5.458
<b>Blue Pencil inlet (C21)</b>															
No.	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mean	3		268.0	-1.0	24.0	244.0	221.5	46.5	16.8	83.1	13.7	25.0	3.72	-5.6	-0.492
<b>Swildon's 4 Inlet upstream of Cowsh inlet (C22)</b>															
No.	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mean	10		269.9	-2.9	27.0	242.9	256.0	13.9	15.2	45.8	11.1	24.3	2.58	-28.5	-1.693
<b>Swildon's 4 Cowsh drip inlet (C23)</b>															
No.	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mean	105		305.8		55.2	250.6	269.0	36.8	73.6	92.3	32.0	75.0	78.0	-3.3	-0.149
<b>Swildon's 5 Damp Link Inlet (C24)</b>															
No.	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mean	0.75		340.8		123.0	217.8	322.0	18.8	37.6	12.8	16.9	40.2	7.4	1.0	0.047
<b>Swildon's 6 Inlet (C25)</b>															
No.	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mean	60		338.8	-1.9	101.4	237.4	325.0	13.8	20.8	34.0	12.3	23.9	3.39	-24.5	-1.171
<b>Swildon's 6 Drip Inlet (C26)</b>															
No.	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mean	2.25		339.8		45.4	294.4	310	29.8	48	40.1	24.4	54.4	10.5	-12.4	-0.567376

**Previous pages: Table 4.** *Characteristics of streams in Swildon's Hole February 1999 to September 2002. Concentrations  $10^5 \times$  Molar, discharge  $l\ min^{-1}$ . Ion balances univalent.*

After the 9 inaccurate data-points had been identified and deleted, there were still 19 samples in the remaining 67 samples where the ion balance errors exceeded  $20 \times 10^{-5}$  M. It was noticed that high IBEs were most frequent in samples from one site, the very small stream draining the south-western segment of Nine Barrows Hill. This stream was often contaminated by cattle grazing a part of this hillside (data shown in Table 1). Apart from this stream, only a small number of samples from the other four surface stream sites gave unsatisfactory ion balances. Conversely, among samples from within the cave, only a small selection regularly yielded low IBEs. These were samples from the main stream throughout the cave, and inlets between the Entrance and Rolling Thunder. In samples from inlets beyond Rolling Thunder, the large majority of samples yielded high IBEs. It was then seen that in the majority of the samples with high IBEs, there was a common factor. Most of them had very high concentrations of nitrate and in these samples, high nitrate levels were often associated with markers of pollution by human or animal waste (elevated levels of sodium, potassium and chloride).

IBEs were extracted from the data tables, together with nitrate levels and new data tables assembled and analysed. New methods for grouping the sites were tried. A different method of grouping the sites for use in the present study will be explained in the section on IBEs in Part 2 of the Results (below).

Among the results from the four relatively uncontaminated surface sites and main stream sites inside the cave, IBEs were considerably lower than in the inlet sites from beyond Rolling Thunder. There remained a small number of samples where the IBEs exceeded  $20 \times 10^{-5}$  M (univalent). In these samples, nitrate levels were higher than usual at the sites involved. It is thought that these cases are likely to have been the result of intermittent grazing of cattle in fields immediately adjacent to the main stream.

## RESULTS:

### 2. STREAMS IN SWILDON'S HOLE

A summary of the results is presented in Table 4, and the sample sites are shown on the plan of the cave, Figure 3. Results in Table 4 reflect the serious effort made by the collecting teams, and the care taken in collecting the data and the samples. The single relative weakness was in the temperature measurements. The electronic thermometers used in most of the trips proved less reliable than expected. Damp penetration several times led to intermittent instrument failure, or, more seriously, to incorrect readings. Because of this weakness, the reliability of temperature data in Tables 1 and 4 is lower than for those obtained in earlier studies using mercury-in-glass thermometers.

In addition to the measurements summarised in Table 4, water samples and/or water temperatures were collected from upstream and downstream of all sampled inlet stream or drip inlets. This was done to allow stream discharge ratios to be calculated by the Method of Mixtures, using data from upstream and downstream of each junction (Stenner and Stenner, 2001). The ratios were then used to calculate absolute discharges. The data from the Main Stream and the inlets were used to produce Figures 7(a), 7(c) and 7(e). These figures show the progressive increase in the total hardness of the main stream and the hardness of the inlets responsible for these hardness changes. Figure 7(a) shows data from a winter trip under high discharge conditions, from the Entrance to Sump 3. Figure 7(c) shows similar data from a

summer trip in lower water conditions. Figure 7(e) shows data from a winter trip in high water conditions, from Swildon's 4, 5 and 6. In Figure 7(e), changes between the Entrance to Sump 3, shown with a dotted line, were estimated. Using the inlet discharge estimates, it was next possible to estimate the increment in the discharge of the Main Stream caused by the progressive addition of the various inlet streams during the course of the Main Stream through the cave from the Entrance to Swildon's 4. This data made it possible to plot the progressive increase in the stream discharge as it flowed through the cave, shown in Figures 7(b), 7(d) and 7(f).

Figures similar to those shown in Figure 7 were plotted for all of the sampling trips made in the cave, but only a selection of these figures are included in this paper. The data from intermediate sites and the remaining figures are included in unpublished data spreadsheet files for every sampling trips, which are available on request to the corresponding author.

If an unknown inlet of significant size had joined the Swildon's Hole streamway upstream of Sump VII, the fact would have been revealed by an unexpected change in the characteristics of the stream. The existence of any such inlet is, therefore, unlikely.

### ***Changes in hardness and discharge in tributary inlets in Swildon's Hole.***

There are three tributary inlets of considerable size in Swildon's Hole. They are the Black Hole Series stream, joining the Main Stream as the "Priddy Pool Passage" inlet not far upstream of Sump I, the North West stream inlet, joining as the Muddy Sump inlet, and the stream from Nine Barrows Swallet and Sludge Pit, joining the Main Stream as the Damp Link Inlet in Swildon's 6 (via Passchendaele). Future detailed studies of these streams would be useful in two respects. Firstly, they would give information concerning inlets close to the points where the water first enters the cave. Secondly they would reveal any situation where water from an unsuspected unknown source joins the inlet. There is some relevant data to support the suggestions.

Site	Total Hardness $10^{-5} \times M \text{ Ca}^{2+}$	Aggress. $10^{-5} \times M \text{ Ca}^{2+}$	Magnesium $10^{-5} \times M \text{ Mg}^{2+}$	Non-Alk Hardness $10^{-5} \times M \text{ Ca}^{2+}$	Chloride $10^{-5} \times M \text{ Cl}^{-}$	Nitrate $10^{-5} \times M \text{ NO}_3^{-}$
Pass. to BH inlet S2	283.1	-16.2	17.9	48.1	26.2	212.9
Well Chamber C11	327	-36.5	17.6	46.5	28.8	70.7
PPP Inlet C10	333.5	-24.1	18.9	46	32	67

**Table 5.** Results from sites in the Black Hole Series on 14<sup>th</sup> February, 1999.

Results from the Black Hole Series, samples from the Well Chamber and PPP inlet were very similar on 14<sup>th</sup> February 1999 are shown in Table 5. The similarity in non-alkaline hardness were particularly significant. This suggests that between these two stations, addition of water from any other source is negligible. The sample from the passage leading to the Black Hole series inlet is difficult to interpret.

Samples from the North West inlet series show the situation here is complicated, and more data is needed here

The sample from the Damp Link inlet in Swildon's 6, which flows via Passchendaele from Nine Barrows Swallet and Sludge Pit, has characteristics (such as total, calcium and alkaline hardness) which are similar to those found in percolation inlets. The one exception was that nitrate levels in this inlet were considerably lower than in any other percolation inlet in the cave beyond Rolling Thunder.

***Comparison of present data with those from earlier studies.***

While Figures 7(a), 7(c) and 7(e) are broadly similar to those reported by Ford (Ford, 1966, *ibid*, p. 47, Figure 11), they differ in one crucial aspect. Apart from the discontinuity he noted at the Priddy Pool Passage Inlet, Ford presented a picture of gradual increase of total hardness resulting from limestone solution by the main stream. He believed that apart from the Priddy Pool Passage inlet, sizes of the percolation inlets were too small to change hardness values in the main stream. The present study, on the other hand, clearly shows stepwise increments of total hardness resulting from mixture with very hard water from various stream inlets, with no detectable limestone solution between successive stations. This situation is similar to that in the Tynning's Swallet stream in G.B. Cave (Stenner, 1973). Although genuine limestone solution has been observed elsewhere in a stream passage (for example in Ogof Ffynnon Ddu (South Wales), Bray, 1975), there has not yet been a similar demonstration in a Mendip cave.

Site	Ford's study		Present study	
	Range	Mean (no.)	Range	Mean (no.)
Drip inlet above Twenty Foot Pot	266		232.6 – 296.7	263.7 (6)
Inlet in Barnes Loop	300		310.3 – 326.5	319.7 (7)
Drip inlet in Tratman's Temple	253		278.1 – 337.1	309.5 (7)
Main Stream upstream of Priddy Pool Passage	<i>134</i> – 260	207 (5)	183.4 – 217.4	200.4 (7)
Priddy Pool Passage inlet	<i>123</i> – 326	244 (5)	331.9 – 348.1	339.7 (7)
Stream in upper Black Hole series	<i>116</i>		283.1	
Stream from North West Stream series	<i>146</i> – 327		343.2 – 356.1	
Main Stream at Sump II	246 – 287	274 (5)	210.9 – 234.7	
Main Stream downstream of Sump III	232 – 316		228.2	
Drip in Blue Pencil passage	326		268.0	
Drip from Cowsh Aven	334		305.8	
Main Stream at Sump IV	308 - 341	326 (5)	231.1	

**Table 6.** *A comparison between total hardness results from Swildon's Hole by Ford (Ford, 1966) and with those from the present study from the same sites. Total hardness in ppm as calcite. Data in italics in Ford's study highlight figures that differ greatly from figures in the present study.*

Ford's data are within the range of the present data at the inlet at the Twenty Foot Pot, and similar to the present data at several other sites. However, at four sites, Ford quotes figures that are considerably lower than data from the present study. Four figures in Ford's list of data

were considered to be particularly significant, and have been highlighted in Table 6, using italics. The possibility that differences in analytical procedures could be responsible for differences were considered. In the present study, the analyses for total hardness were completed within twelve hours of collection, whereas Ford stated that most of his samples were titrated in two to seven days of collection. This is insufficient to account for the differences between the data sets. Although some of the sampling trips in the present study took place when stream discharge was high, it is possible that some of Ford's samples were collected in highly abnormal stream conditions. It will be important to try to clarify this position, because the magnitude of the discrepancy between the two sets of data is so great. This matter is very important because it is possible that under the extreme conditions of at least one of Ford's collection trips, a completely different water-flow pattern was operating in some parts of the cave. To be more specific, it seems possible that in two parts of the cave, namely the Black Hole Series and the North-west Stream series, the normal percolation water regime was invaded by storm water from the surface bypassing the normal stream routes. Clarification of this point is important for a full understanding of the hydrology of the cave.

***The possibility that stream inlets in Swildon's Hole might be derived from the main surface stream.***

As had been explained above, comparisons were made between the non-alkaline hardness and certain other stable solutes, in the surface stream and those in inlet streams in the cave. The purpose was to use the proposed criteria to ascertain whether other inlets in the cave could or could not have been derived from the main stream at the surface (Stenner and Stenner, 2001).

The principle was applied to the sets of data collected in seven sampling trips in Swildon's Hole. Samples from the 6 inlets between Rolling Thunder and Sump 1 gave a consistent pattern. All 29 samples had a much higher nitrate content than the surface stream, and 28 of the 29 samples had a considerably higher non-alkaline hardness. The patterns for chloride, sulphate, sodium and potassium were more variable, but there was an overall lack of similarity between the levels in the inlets and those in the surface stream. The conclusion is that these streams are completely independent of the main stream at the surface.

Next, data from inlets closer to the entrance were examined. They were from the Water Chamber, the stream flowing from the Old Grotto, and the Rolling Thunder inlet stream. The data from these sites showed many striking similarities with the main stream at the surface. There were increments of total hardness, alkaline hardness and aggressiveness, as would have been predicted from earlier work here and in St. Cuthbert's Swallet (Bridge *et al*, 1977). Of particular significance, changes of non-alkaline hardness were small, and close to the analytical precision, in every sample that was analysed completely. Some of the samples of water from the Old Grotto showed clear signs that they had been contaminated (elevated chloride and nitrate). This does not weaken the suggestion that the Old Grotto stream and the Rolling Thunder inlet are derived from the surface stream, with negligible addition of water from any other source. For this reason, the volume of the Main Stream below Rolling Thunder has been assigned the same value as the main stream on the surface.

Finally, samples were collected from 14 inlets downstream of Sump 1, as far as two inlets in Swildon's 6. In the case of 12 of these inlets, large differences in non-alkaline hardness prove that the samples are not connected with the surface stream. In one of the remaining inlets, a greatly different magnesium content eliminates any such possible connection. The remaining

sample, the inlet upstream of Cowsh Inlet in Swildon's 4, has levels of magnesium too high for connections with the surface stream to be feasible.

To sum up, the intermittent stream flowing through the Upper Series and the Old Grotto is certainly an offshoot of the main stream at the surface. Similarly, the Rolling Thunder inlet has characteristics (non-alkaline hardness, chloride, sulphate, sodium and potassium) which are similar to those in the surface stream, strongly suggesting that this inlet is also derived very largely, if not totally, from the surface stream. The situation with all of the inlets after Rolling Thunder is completely different. Without exception, they all have very high total hardness, and it has been possible to show that they have no connection with the main stream on the surface. These inlets may be categorised as "percolation water".

#### *Characteristics of inlet drip and trickle streams.*

The most frequently sampled inlet sites, the 6 percolation inlets between the Forty Foot Pot and Sump I, are listed in Table 4. More limited data are available from 8 percolation inlets beyond Sump 1, and from 6 further percolation inlets between Swildon's 4 and Swildon's 6 and these are also listed in Table 4. We note that the variability of total hardness in most inlets was low, in contrast with the high variability of total hardness in the unpolluted surface streams. Similarly, variabilities of calcium and alkaline hardness were low in the inlet streams. Water temperatures in the inlet waters were considerably more variable than in the G.B. study, undoubtedly because most water temperatures were measured far from the points where the inlets entered the open cave. This distance is also believed to have been responsible for the unusually high variability of aggressiveness that has been noted previously. This result will be discussed in more detail below. The low variabilities of total, calcium and alkaline hardness are a strong indication that in the upstream space between the point where the stream enters the cave and the subsoil, air carbon dioxide concentrations must be very stable.

The high alkaline hardness in percolation water will be stable only when the water contains enhanced concentrations of dissolved carbon dioxide (Picknett *et al*, 1976). When surrounded by air containing normal atmospheric levels of carbon dioxide, such water will degas carbon dioxide into the cave air, becoming supersaturated with dissolved calcium hydrogen carbonate, thereby gaining the ability to deposit calcite. Aggressiveness data are therefore highly relevant.

In addition to high total hardness, some of the inlets have characteristics that warrant discussion. Compared with surface streams, many of the constituents have very low variabilities. These are shown in Table 4 by the standard deviations and the Relative Standard Deviations (RSDs). In the present study, many inlets were sampled a considerable distance from the sites where the inlets emerged into the open cave. In a previous study in G.B. Cavern, care was taken to sample many of the inlets as close as possible to the points where they emerged into the cave. In the G.B. study, the data for the aggressiveness of the inlet trickles showed much less variability than is shown in the present study. It is suggested that if inlet trickles and drips were to be sampled close to their points of emergence into the cave, the variability in the aggressiveness will turn out to be much lower than the data presented here. This suggestion has not yet been tested.

The data for the Rolling Thunder inlet is very interesting. The total hardness has a very low variability. This shows that although the water in this inlet is derived from the surface stream, it had flowed through a zone between the surface and the inlet, where carbon dioxide levels were higher than in the open atmosphere, and stable. This caused the water to achieve increased levels of total and alkaline hardness and calcium and these levels were stable.

While the non-alkaline hardness of samples has proved to be useful for diagnostic purposes, the measurement in itself is not an obviously useful property of water.

In samples collected downstream of the Rolling Thunder inlet, from the 6 frequently sampled sites and 14 further infrequently sampled inlet sites, the following noteworthy features were found.

1. Nitrate levels were high in water from every site except one (the Damp Link Inlet stream in Swildon's 5). Some of the nitrate figures were remarkably high ( $311 \times 10^{-5}$  M at the Muddy Sump inlet,  $220 \times 10^{-5}$  M upstream of Wet Ears Squeeze,  $203 \times 10^{-5}$  M in the inlet in the passage to the Black Hole). In all samples with nitrate levels above  $75 \times 10^{-5}$  M, ion balances were unsatisfactory.

2. Chloride levels were above  $100 \times 10^{-5}$  M at three sites (upstream of Wet Ears Squeeze, the Muddy Sump inlet and the 1<sup>st</sup> Mud Sump), and  $73.6 \times 10^{-5}$  M in the Cowsh Inlet in Swildon's

4. Chloride levels were also unusually high in the Priddy Pool Inlet, the Damp Link inlet, and the Swildon's 6 drip inlet.

3. Magnesium levels were highly unusual at some sites ( $123 \times 10^{-5}$  M in the Damp Link Junction Inlet in Swildon's 5,  $101 \times 10^{-5}$  M in the Swildon's 6 inlet,  $55 \times 10^{-5}$  M in the Cowsh inlet in Swildon's 4,  $45 \times 10^{-5}$  M in the drip inlet in Swildon's 6,  $36 \times 10^{-5}$  M upstream of Wet Ears Squeeze,  $32 \times 10^{-5}$  M in the Muddy Sump inlet, and  $32 \times 10^{-5}$  M at Caliper Pot). In some of these cases, there seems to be small "clusters" of inlets with higher magnesium than is usual. It is suggested that the water feeding these inlets may have flowed through local residual deposits of Triassic Conglomerate.

4. Sodium levels were grossly high in some sites ( $240 \times 10^{-5}$  M in the 1<sup>st</sup> Mud Sump,  $190 \times 10^{-5}$  M in the Muddy Sump inlet). They are also higher than usual in all the sites mentioned previously as having unusually high chloride levels.

5. Potassium levels were very much higher than usual at a number of sites ( $78 \times 10^{-5}$  M in the Cowsh Inlet,  $55 \times 10^{-5}$  M in the Muddy Sump Inlet,  $28 \times 10^{-5}$  M upstream of Wet Ears Squeeze). Levels were lower than these highly abnormal figures, but still notably enhanced, in the Priddy Pool Inlet, the inlet in passage to the Black Hole, Caliper Pot, and in the drip inlet in Swildon's 6.

6. In the six inlets from below Rolling Thunder to Sump 1, a very high proportion of samples gave results with unusually high ion balance errors.

*Percolation water: the problem of definition.*

Some inlets have been referred to above as "percolation water". There is no rigorous method for dividing inlet streams into categories that can be applied rigidly in all cases. In St. Cuthbert's Swallet, many small trickles with characteristics of percolation inlets (stable physical/chemical properties) turned out to be derived entirely from a surface stream. In the present studies, the Damp Link stream inlet in Swildon's Six flows from two small swallet streams (Nine Barrows Swallet and Sludge Pit Hole). By the time this stream joins the main stream, it is strikingly similar to the stream that flows from the North-west Stream Passage, and to the Black Hole Series stream. Both of these two last-named streams are thought to have no swallet water component. All three streams can be followed for a considerable distance from

their respective main stream junctions upward towards the surface, and are therefore inlet streams that are suitable for further detailed study in the future.

### ***Ion balance errors (IBEs) in the present study, and their causes.***

Ion imbalances found in many samples, reflected in Tables 1 and 4, were far too high to have been caused by the measured imprecision of the analytical methods ( $15.3 \times 10^{-5}$  M univalent). The possibility that high levels of ammonium ions were responsible, especially as there were often too many negative ions, was investigated. Many samples were analysed for ammonium ions using Nessler's Reagent, and in every case ammonium levels were below 1ppm (equivalent to  $7.14 \times 10^{-5}$  M  $\text{NH}_4^+$ ). From these results it was concluded that ammonium ions were unlikely to be present in significant concentrations, and no further analyses for ammonium were carried out, and other causes of the IBEs had to be sought. An important observation was the fact that so many samples from small stream inlet sites gave very large IBEs.

As explained above, a rigorous discussion of IBEs has been left until now as the large majority of samples with high IBEs came from sites downstream of Rolling Thunder.

The theoretical overall standard error of the IBE in the present study, calculated from the standard error of each analytical method, was  $15.3 \times 10^{-5}$  M (univalent), compared with  $6.32 \times 10^{-5}$  M (univalent) in the St Cuthbert's study. This difference is noted, because it shows the consequence of relatively minor changes of analytical routines on the precision of analytical data.

The number and magnitude of the ion imbalances were unexpected, and a very unwelcome surprise. The IBEs in the present study were compared with those in the St. Cuthbert's Swallet study (Knights and Stenner, 1999, Table 2). The ion balance error had been greater in percolation water inlets, Pyrolusite Series, the former Plantation Stream at Plantation Junction and the Kanchenjunga drip, than in the remaining samples from St. Cuthbert's Swallet. The IBEs in the 9 samples from the percolation water samples that were analysed completely were, apart from a single sample, relatively high. Nitrate values were also high. Statistical summaries were calculated of nitrate levels and of ion balances in data from inside St. Cuthbert's Swallet. Similar summaries were calculated for the data after deleting the data from the three percolation sites. Nitrate mean levels fell from  $12.7 \times 10^{-5}$  M (91 analyses, SD 12.7) to  $9.9 \times 10^{-5}$  M (82 analyses, SD 6.3). IBE mean values fell from  $-1.0 \times 10^{-5}$  M univalent (53 analyses, SD 5.1) to  $-0.8 \times 10^{-5}$  M (44 analyses, SD 4.6). This analysis showed that the three percolation inlets contained higher levels of nitrate than the other sites in the cave, and removing these sites from the database reduced the standard deviations of the IBEs. However, the IBEs in the samples were relatively low. The highest value was  $11.4 \times 10^{-5}$  M (univalent).

The overwhelming conclusion after comparing the present study with the St. Cuthbert's study, however, was this. While in the latter study, identifying the consequences of experimental mistakes was important in increasing the overall precision of the data, identifying experimental mistakes was relatively unimportant in the present study. In this study, IBEs were largely the result of a fundamentally different process or processes.

IBEs were tabulated, scrutinised and analysed. No serious mistakes were identified among results from samples collected within the cave. However, a high proportion of the samples showed high ion balance errors. In the 33 samples that were analysed completely, 5 had an IBE > 5%; 15 had an IBE >  $30 \times 10^{-5}$  M; 20 had nitrate levels >  $50 \times 10^{-5}$  M. However, certain sites within the cave yielded data from which a small proportion had poor ion balances. From 18 samples from inside the cave (from the Old Grotto, Rolling Thunder, and Main Stream

sites), only 2 samples had an IBE  $> 20 \times 10^{-5}$  M, No sites had an IBE  $> 5\%$  or  $> 30 \times 10^{-5}$  M, and no sites had nitrate levels  $> 50 \times 10^{-5}$  M. Water from the Rolling Thunder site has previously been shown to have been largely derived from the surface stream. The six inlets downstream of Rolling Thunder as far as Sump 1, which yielded such a high proportion of high IBEs, all showed the chemical marker of contamination by human or animal waste (unusually high levels of nitrate, chloride, sodium and potassium). This situation differs sharply from that in the surface stream sites (*Results 1*), where only samples from the Nine Barrows surface drainage stream frequently showed the chemical markers of contamination by human or animal waste.

Beyond Sump 1, samples were divided into two clear groups; those from the main stream with few poor ion balances, and those from percolation water inlets, with a very high proportion of samples having poor IBEs. Although the percolation inlets beyond Sump 1 were not tested for the presence of gut bacteria, they showed the same chemical markers (high levels of sodium, potassium, chloride and nitrate) as the contaminated inlets in Swildon's 1, in which the presence of presumptive *Coliform* bacteria was confirmed.

In other studies, some samples from Wookey Hole Cave, the Axe and other South Mendip springs contained semi-stable suspensions of "colloidal" calcite, and these samples yielded grossly unsatisfactory ion balances. Suspensions of calcite and the analytical difficulties they cause calcite have been discussed elsewhere (Chapman *et al*, 1999). Calcareous suspensions were proved to have no part in the IBEs found in the present study. Acidification of samples had no effect, which was the case in the samples from Wookey Hole Cave and several other similar sites. However, colloidal suspensions of a different origin were found to have a link with IBEs in the present study, and this will be discussed below.

The common factor in the samples from Swildon's Hole with a large IBE, from Nine Barrows Hill local drainage stream, and inlets from downstream of Rolling Thunder, was the fact that they contained high concentrations of nitrate. Indeed, it became evident that the higher the nitrate content was, the more serious the ion imbalance was likely to be. In most of these samples, levels of chloride, sodium and potassium were also unusually high, leading to the conclusion that these samples were likely to be contaminated by human or animal waste. This suspicion was later confirmed by results from two sampling trips made in 2001 and 2002, when tests were made to detect gut bacteria in suspect inlets (discussed below).

The analysis of ion balance errors discussed in the previous paragraphs prompted Stenner to divide the samples into two distinct groups:

Group 1. Those sites from relatively unpolluted surface streams, main stream sites within the cave, and substantially unpolluted inlets.

Group 2. Sites with chemical markers of seriously contamination by human or animal waste, and sites where earlier workers had proved contamination by such waste to be present.

The ion balances were tabulated according to these criteria. The resulting table is not included here but a copy can be obtained from Stenner or from the editor of the UBSS.

The IBE results show a very clear division of the results into two groups.

From sites with low pollution levels:

84 samples yielded 65 results where IBE  $< 20 \times 10^{-5}$  M (77.4%); 7 results where IBE  $> 30 \times 10^{-5}$  M (8.3%); 0 results where IBE  $> 50 \times 10^{-5}$  M; 3 results where IBE  $> 5\%$  (3.6% of the samples).

From the sites with high pollution levels:

56 samples yielded only 21 samples where  $IBE < 20 \times 10^{-5} M$  (37.5%); 23 results where  $IBE > 30 \times 10^{-5} M$  (41.1%); 14 results where  $IBE > 50 \times 10^{-5} M$  (25.0%); 10 results where  $IBE > 5\%$  (17.9% of the samples).

Figures for ion balance error (IBE) are  $10^{-5} \times M$  (univalent). Figures for nitrate concentrations are  $10^{-5} \times M NO_3^-$ .

This analysis showed that in the contaminated inlets downstream of Rolling Thunder, the very high proportion of IBEs is associated with problems connected with high nitrate concentrations, rather than with analytical inaccuracies.

#### ***Colloidal suspensions and ion balance errors.***

There was a common factor in samples from contaminated sites in this cave and those from other sites affected by colloidal calcite. Several samples in the present study showed the presence of colloidal suspensions. Many of the samples were coloured, and the coloration was not removed by filtering the sample through a Whatman No. 540 filter paper. Some of the samples became cloudy after "salting" with a spatula-measure of AnalaR sodium chloride, and others became cloudy after boiling briefly, supporting the suspicion that colloids were likely to be implicated in this analytical problem. The colloids did not have any effect on total hardness or alkalinity titrations, so they were different from the colloids which were sometimes encountered in, for example, the River Axe at Wookey Hole Cave (Chapman *et al*, 1999). This fact shows that while colloids were likely to have been a factor in the Swildon's Hole samples they were not "colloidal calcite". The following possibility is suggested; large concentration of nitrate in the polluted samples may have been associated with cations bonded to organic macromolecules unavailable to the normal techniques of the water analyst.

#### ***Indications of pollution in inlet streams.***

A striking feature in Table 4 is the fact that there are such clear indications that many of the inlet streams are polluted. Concentrations of potassium, sodium, chloride and nitrate are often significantly higher than those found in unpolluted natural water. It has long been known that the Priddy Pool Passage inlet stream was polluted by human sewage (Manley and Taylor, 1978). Cowsh Aven in Swildon's IV carries water from Priddy Green Sink and is quite obviously frequently seriously contaminated with cattle waste. However, the very poor water quality in so many inlets in the cave was unsuspected. In fact, after the Rolling Thunder inlet, few of the inlets sampled did not show abnormal chemical features. The presence of high levels of sodium, potassium, chloride and nitrate together in so many samples suggests very strongly that these inlets are contaminated by human or animal waste.

Because of the suggestion that so many of the inlets were seriously contaminated, it was thought to be prudent to carry out further sampling of these inlets, to determine whether intestinal bacteria are present. Two sampling trips were made, one in winter when the stream was at normal, quite high, winter levels and one in summer soon after the surface stream stopped flowing. The trips took place on 23<sup>rd</sup> December 2001 and 5<sup>th</sup> September 2002. Details of the sampling procedure have been described previously.

Description	23/12/01				5/09/02			
	Temp °C	Pres. coliform	Pres. coliform	Mean Pres. coliform	Temp °C	Pres. coliform	Pres. coliform	Mean Pres. coliform
Date								
Rolling Thunder inlet	8.4	>2000	>2000	>2000	9.8	15	10	12
Drip d/s Rolling Thunder	9.3	>1000	>1000	>1000	Dry			
Inlet above 20' Pot	9.2	>1000	>1000	>1000	Dry			
Inlet in Barnes' Loop	9.5	>1000	>1000	>1000	9.6	0	0	0
Inlet in Tratman's Temple	9.9	700	700	700	10.2	125	150	137
Inlet below Trat's Temple	9.6	444	300	370	9.6	1405	1175	1290
Priddy Pool Passage inlet str.	9.8	150	100	125	9.8	90	275	182
Main Stream at Sump I	8.8	475	575	505	9.8	135	50	92
Unused plates		0	0	0		0	0	0

**Table 7.** Gut bacteria (presumptive Coliform bacteria in inlet streams and trickles between Rolling Thunder and Sump I in high water in winter, and low water in late summer. Determined by culturing bacteria by inoculating MacConkey Agar plates (prepared and supplied by Oxoid Ltd., Basingstoke) in situ with 0.2 ml water, and incubating at 38°C.

The results of the counts are presented in Table 7. At every site the counts from the two plates agreed with each other as well as may be expected in this type of study. Unused plates were the controls, and in every case no colonies appeared after these plates were incubated alongside the used plates. The results confirm that in winter conditions, every inlet between Rolling Thunder and Sump I was contaminated with gut bacteria. This result amplified and clarified the earlier studies by Bacon *et al.*, (1963) and by Manley and Taylor (1978). The counts in the summer samples were much lower than the winter counts (as they normally are in surface streams and rivers), and some of the inlets were completely dry. The results justify the decision to culture gut bacteria rather than using the methods used by Freiderich *et al.* (1982) in G.B. Cave.

### ***The aggressiveness of inlet streams.***

The data concerning aggressiveness to calcite has proved to be particularly important. When inlet sites in G.B. Cave were sampled in 1968, many of the small inlets were sampled very close to the points where the water emerged into the cave atmosphere. This ensured that the chemistry of the samples was as close as possible to the chemistry of the water within the limestone, before it could be influenced by contact with the cave atmosphere. This approach was not feasible in the present studies, and most samples were collected far from the points where the water first emerged into open cave. The data would therefore detail the capacity of the water to dissolve or deposit calcium carbonate at points fairly close to where the inlet streams merged with the Main Stream.

The data showed quite clearly the same trend at every cave inlet site that was regularly sampled: the inlets were found to be strongly supersaturated in the winter months (November to March, included) and either much less supersaturated or slightly aggressive in the summer months (May to September included).

The first attempts to assess the variability of aggressiveness data were of limited usefulness, because the relative standard deviations were unusually high, and usual comparisons were not easy to interpret. Another method for assessing the seasonal trend in aggressiveness, used in the study in G.B. Cave (Stenner, 1974) was tried. In the G.B. studies, tabulating the total hardness of the saturated samples had been useful at most sites. At two sites in that study the saturated total hardness was actually less variable than the total hardness. At the three major stream sites and the remaining 8 percolation water sites inside G.B. Cave, standard differences in total hardness and saturated total hardness were small. This showed that changes in variability of the two properties at the majority of sites in that cave, changes that would have been caused by the variations in aggressiveness, were small. This was a reflection of the unusually highly variable aggressiveness.

Similar comparisons, between total hardness and saturated total hardness, were calculated for data from the St. Cuthbert's Swallet studies and from the present study. Both the Fair Lady Well study and the right pipe stream from the Bristol Water compound had very low variability for both quantities, shown by figures for standard deviations and relative standard deviations. But additionally, in both of these cases, differences between the variability of total hardness and that of saturated total hardness were small. But among the 7 inlets streams and trickles from Rolling Thunder to Sump I, the pattern was different and the following differences were noted for the variability of the total hardness compared with that of the saturated total hardness. At the Rolling Thunder inlet the S. D. increased from 5.45 in the unsaturated samples to 15.01 in the saturated samples. At the Barnes Loop inlet the increase was from 6.89 to 18.62. At the Priddy Pool Passage inlet the increase was from 5.92 to 14.51, and at the drip

inlet in Tratman's Temple the increase was from 18.59 to 32.85. At the other three drip inlets, there were smaller increases. The large increases were caused by greatly enhanced variability in the saturated total hardness. This was caused by highly variable aggressiveness. There was the same trend at all seven frequently sampled inlet stream sites. The trend is for the saturated total hardness to have a greater variability compared with total hardness patterns. Such a trend was absent in data from G.B. Cave, and in the surface data from St. Cuthbert's Swallet.

#### *A seasonal pattern of aggressiveness of inlet streams.*

The increase in the variability in the saturated total hardness in the inlet streams, a reflection of much greater variability in aggressiveness, was examined in greater detail. Aggressiveness during winter months, November to March inclusive, was more negative (supersaturated) than during summer months, May to September inclusive. In fact at several sites, inlet water was usually aggressive to calcite during summer months. At four of the seven regularly sampled sites between the Forty and Sump 1 (the Rolling Thunder inlet, the inlet upstream of The Twenty, the Barnes Loop inlet and the Tratman's Temple inlet), the division between the winter and summer data was 100%. At each of the remaining three sites only a single data-point at each site did not follow this pattern. For example, at the Tratman's Temple site, the three winter samples had aggressiveness values of -28.5, -32.5 and -19.9 ppm as calcite and the four summer values were +2.8, +0.9, +5.8 and +8.6 ppm as calcite. Altogether, 43 out of 46 aggressiveness measurements followed this seasonal trend at the seven inlet sites.

#### *Explaining the seasonal aggressiveness changes.*

Interpreting the aggressiveness data needs caution. Discussing the mathematics of the calcite/water/CO<sub>2</sub> system (Picknett *et al.*, 1976) is beyond the scope of this paper, but the consequences of the theories have been discussed in the Introduction. Applying the theory to the present study gave definite conclusions. At most inlet sites, there was very little difference in total hardness between summer and winter. This shows that within the limestone, from the soil/limestone boundary where the water entered the limestone to the point of emergence into the cave, the dissolved calcium hydrogen carbonate concentration is fairly constant. The direct consequence of this observation is that the dissolved carbon dioxide content of the water within the limestone must also be constant. In every case, the inlet water within the limestone can also be expected to follow the same patterns that were found in G.B. Cavern and St. Cuthbert's Swallet, and arrive at the open cave at a constant temperature, independent of season.

If the air into which the inlet emerges had a constant carbon dioxide level, seasonal aggressiveness changes would have to be explained by the calcite/water/carbon dioxide system. But if this were the case, supersaturation would be at a minimum in winter and a maximum in summer. This is because carbon dioxide is more soluble in cold water than in warm water, and in summer the trickles would be warming up as they flowed through the cave. This is the exact reverse of the observed state. It is our conclusion that the calcite/water/carbon dioxide system cannot be the driving force for the observed aggressiveness changes. Since the cave air cannot have a constant carbon dioxide level, we propose that to produce the observed aggressiveness change from summer to winter states, the concentration of carbon dioxide in the air around the inlet stream must have been higher in summer than in winter. We propose this as the simplest and the most likely explanation of the aggressiveness data.

### ***Poor air quality in Swildon's Hole.***

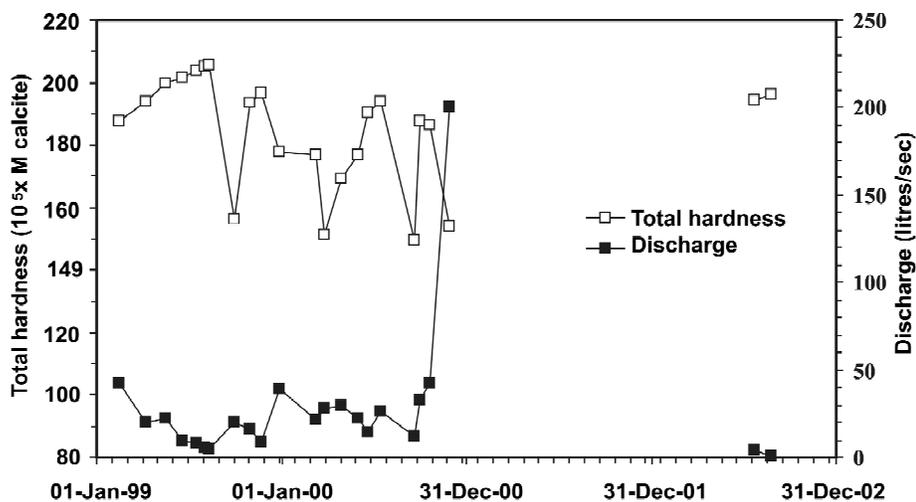
The aggressiveness phenomenon described here is certainly related to a problem of poor air quality reported for Swildon's Hole in *Descent* magazine in 1993 and 1994 (Glanville, 1993). In the same issue in which it was reported that an inlet in the cave was reported to have been polluted by light diesel oil (Sparrow, 1993), air quality in the cave was also discussed in another letter. It was reported (Glanville, 1993) that in drought conditions, the entire Swildon's Hole system became stuffy. In normal water level conditions the problem was restricted to parts of the Shatter Series, especially the Wet Link to Swildon's VI, Paradise Regained, St. Paul's Series, North-west Passage and the Inlet Dig in Swildon's VII. He added "current wisdom has it that high carbon dioxide levels and low flow are linked...organic materials...are decaying in the passages below and generating carbon dioxide. With poor stream flow the gas is not dissolved and carried away" (Glanville, 1993). The water resource manager of the National Rivers Authority, SW Region replied "more intensive farming will have a major effect on ground water and a knock-on effect on cave air as organic materials oxidise" (Newman, 1994).

### ***The origins of aggressiveness changes.***

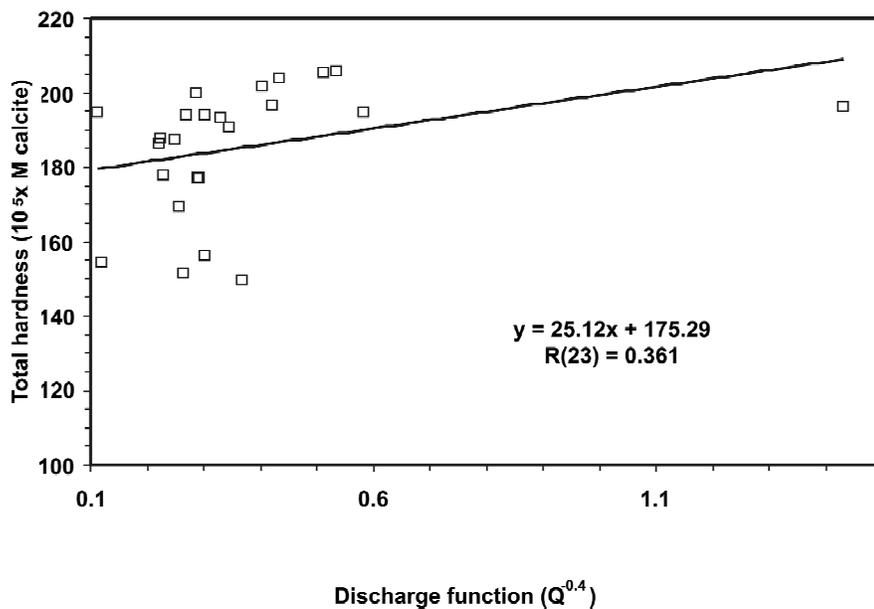
The *Descent* articles in 1993 and 1994 were written after a sequence of dry summers, whereas present aggressiveness data come from unusually wet summers when there has been no pumping from Priddy borehole, and the stream discharge values were high. Having showed that carbon dioxide was not carried into the cave in solution, the question of the actual source of the carbon dioxide in the cave air remains. Preliminary calculations rule out generation by respiration of cavers. Present data suggest stream-borne human or animal waste as a possible origin. The wide range of unusual chemical markers, enhanced levels of sodium, potassium, chloride and nitrate, suggests that the contamination was caused by domestic or animal waste rather than synthetic fertiliser. In the case of pollution by a synthetic fertiliser, enhancement would have been restricted to a limited number of chemical markers (Manley and Taylor, 1978). It is tempting to suggest a role for bacterial oxidation of the organic matter in the cave. Bacterial activity is slower below 12°C than at a higher temperature. However, studies at St. Cuthbert's Swallet have shown that during anticyclones, surface air can be detected considerable distances underground. In summer, this air will be considerably warmer than ambient cave air (Stenner and Picknett, 1999), and this could be an important factor in the generation of carbon dioxide gas. This is an important area for future cave research, in which remote instrumental monitoring will be required.

While the need for further research is clear, it is a matter of some satisfaction that reports of poor air quality in the cave, (Glanville, 1993), are consistent with this new water aggressiveness data, with clearly demarcated seasonal patterns. This result is more striking considering the fact that most of the present data were collected in two unusually wet summers. It is anticipated that this seasonal trend will be even more pronounced in years when more normal dry summers occur.

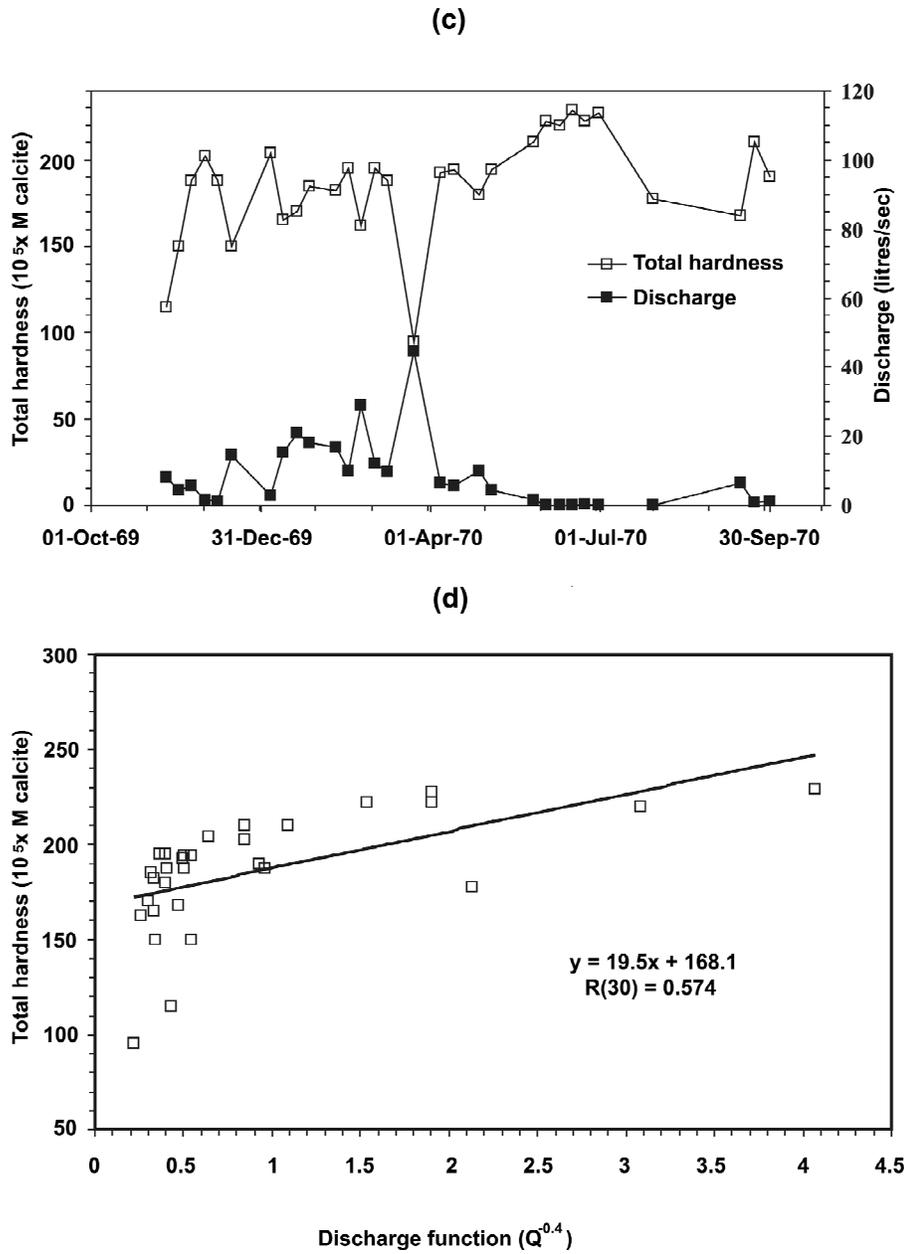
(a)



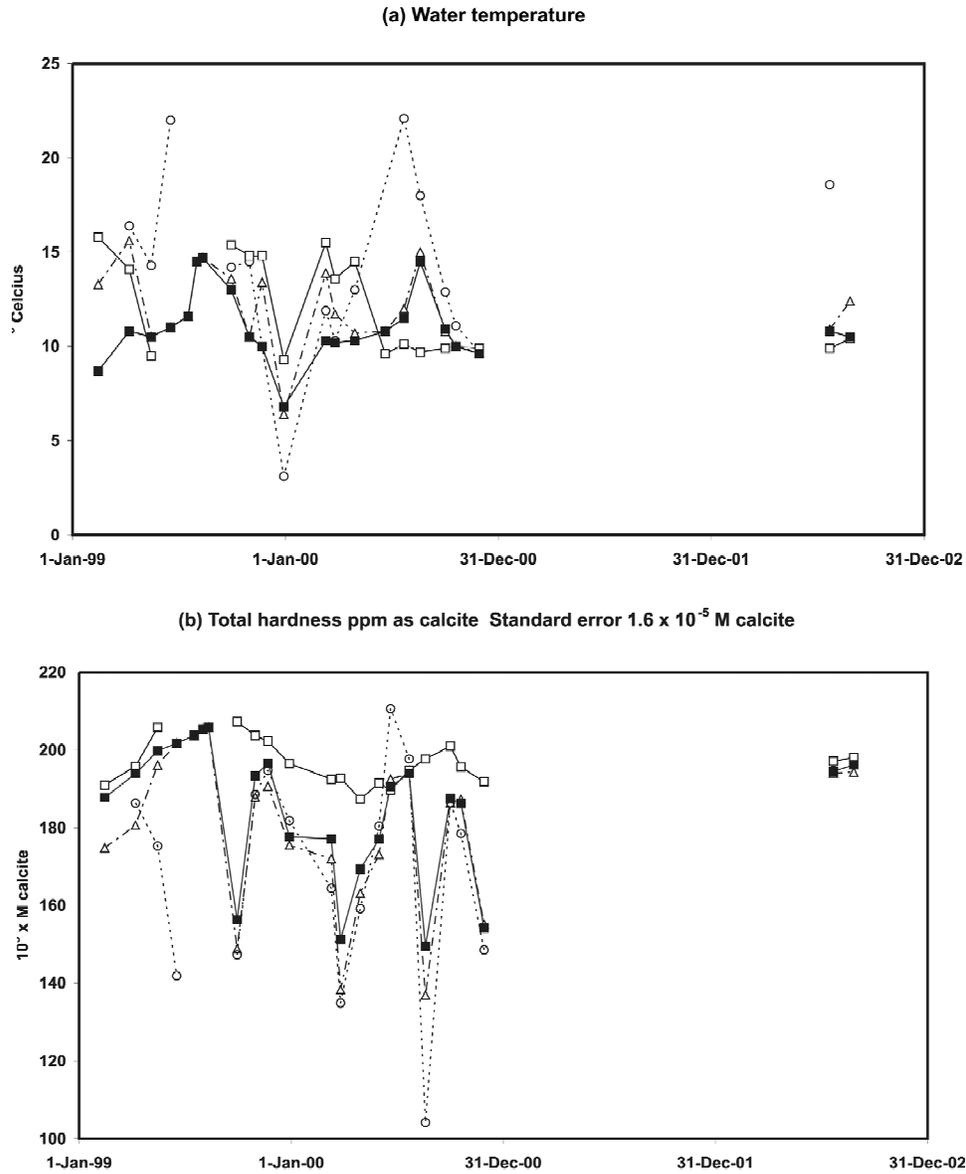
(b)



**Figure 4.** (a) Total hardness (ppm as calcite) and stream size (litres per minute) at the Swildon's Hole Stream at the Cave Entrance from February 1999 to September 2002. (b) The relationship between total hardness (ppm as calcite) and stream size (litres per minute) at the Swildon's Hole Stream at the Cave Entrance, February 1999 to September 2002.

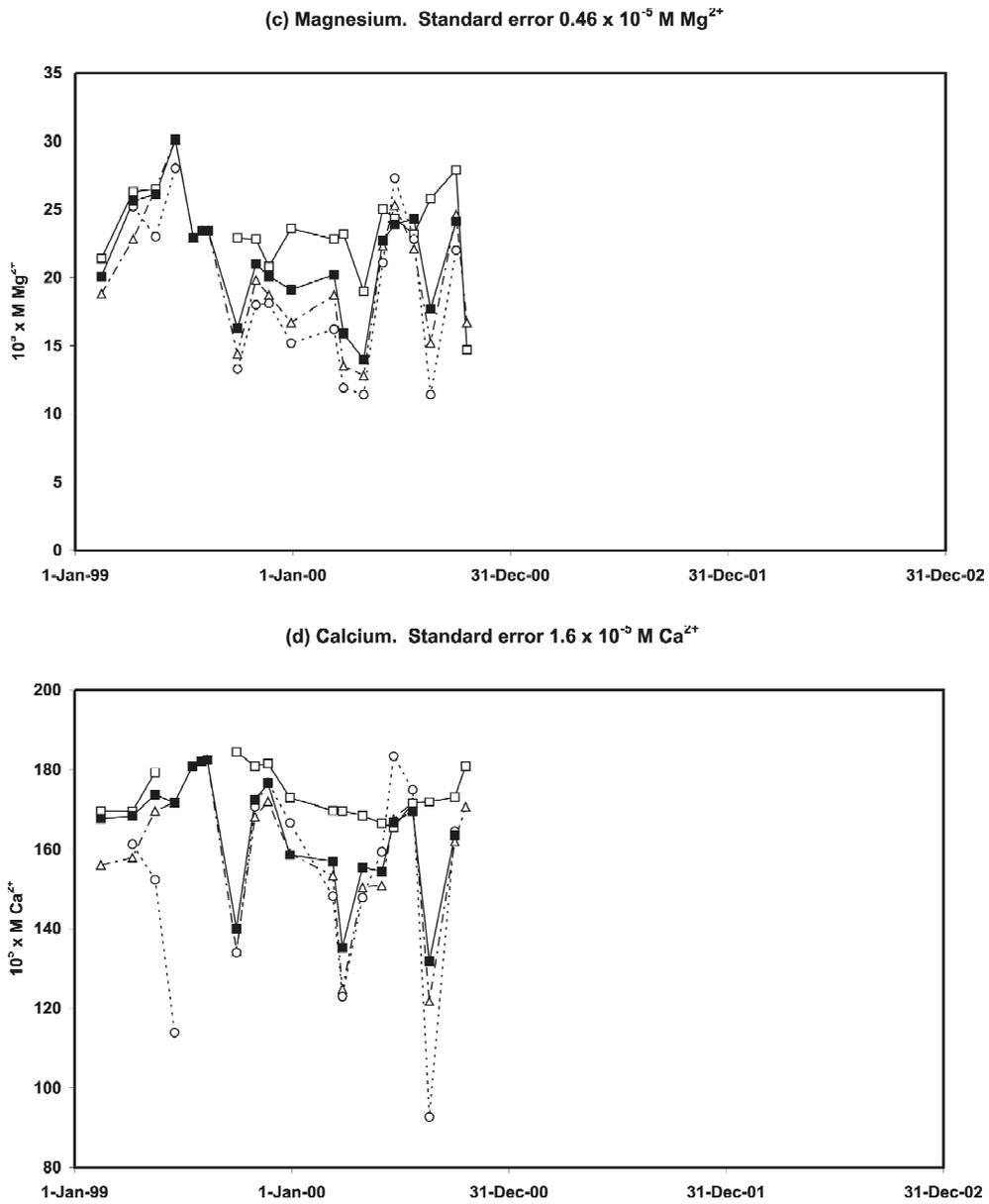


**Figure 4.** (c). Total hardness (ppm as calcite) and stream size (litres per minute) at the Swildon's Hole Stream at the cave entrance from Nov. 1969 to Sep. 1970. (d). The relationship between total hardness (ppm as calcite) and stream size (litres per minute) at the Swildon's Hole Stream at the cave entrance, Nov. 1969 to Sep. 1970. All data by Atkinson.



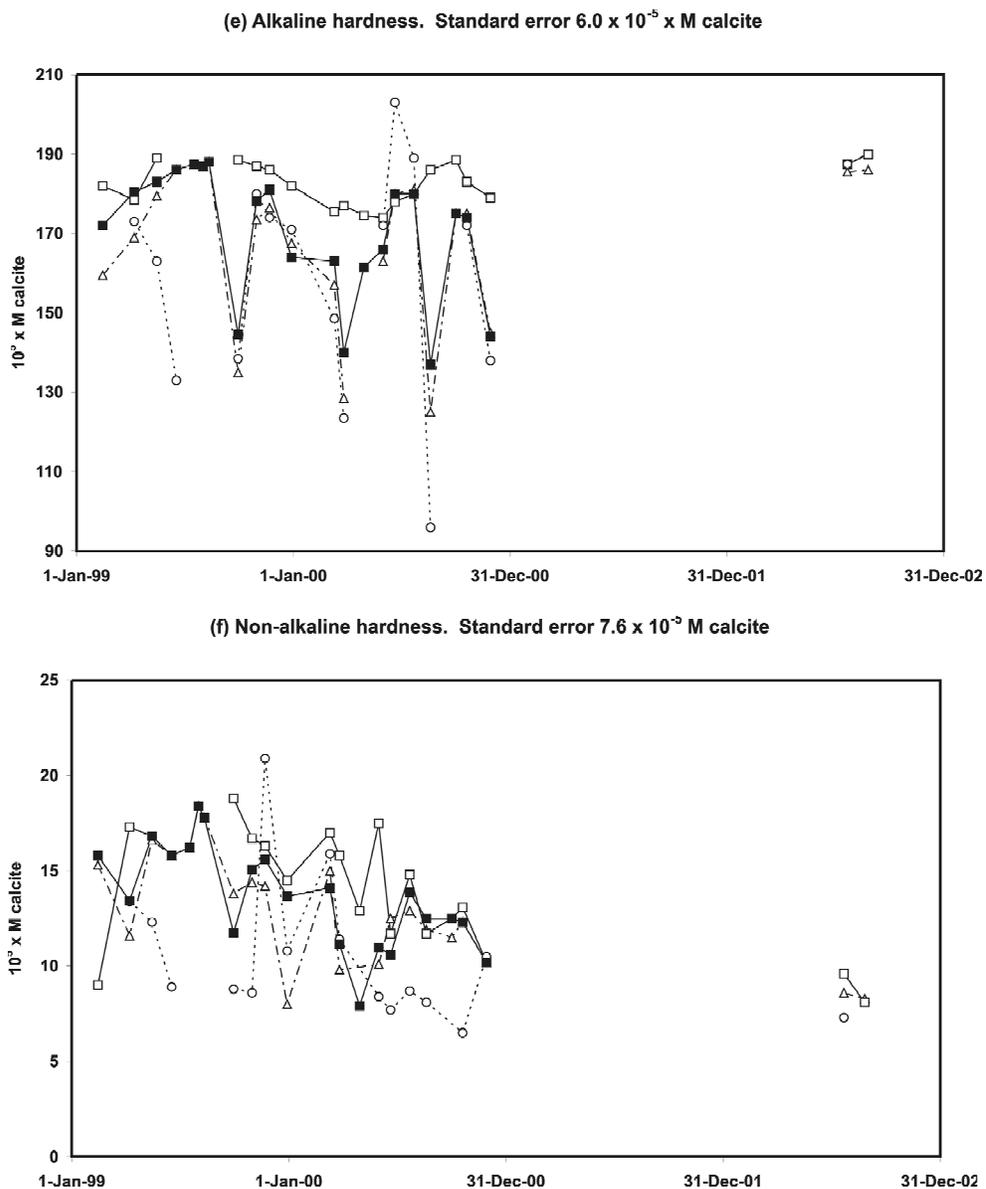
**Figure 5.** (a) Water temperature ( $^{\circ}$  C) at four sites, February 1999 to September 2002. (b). Total hardness (ppm as calcite) at four sites, February 1999 to September 2002.

■ = CI; ○ = Priddy Pool outlet stream; △ = left pipe stream; □ = right pipe stream.



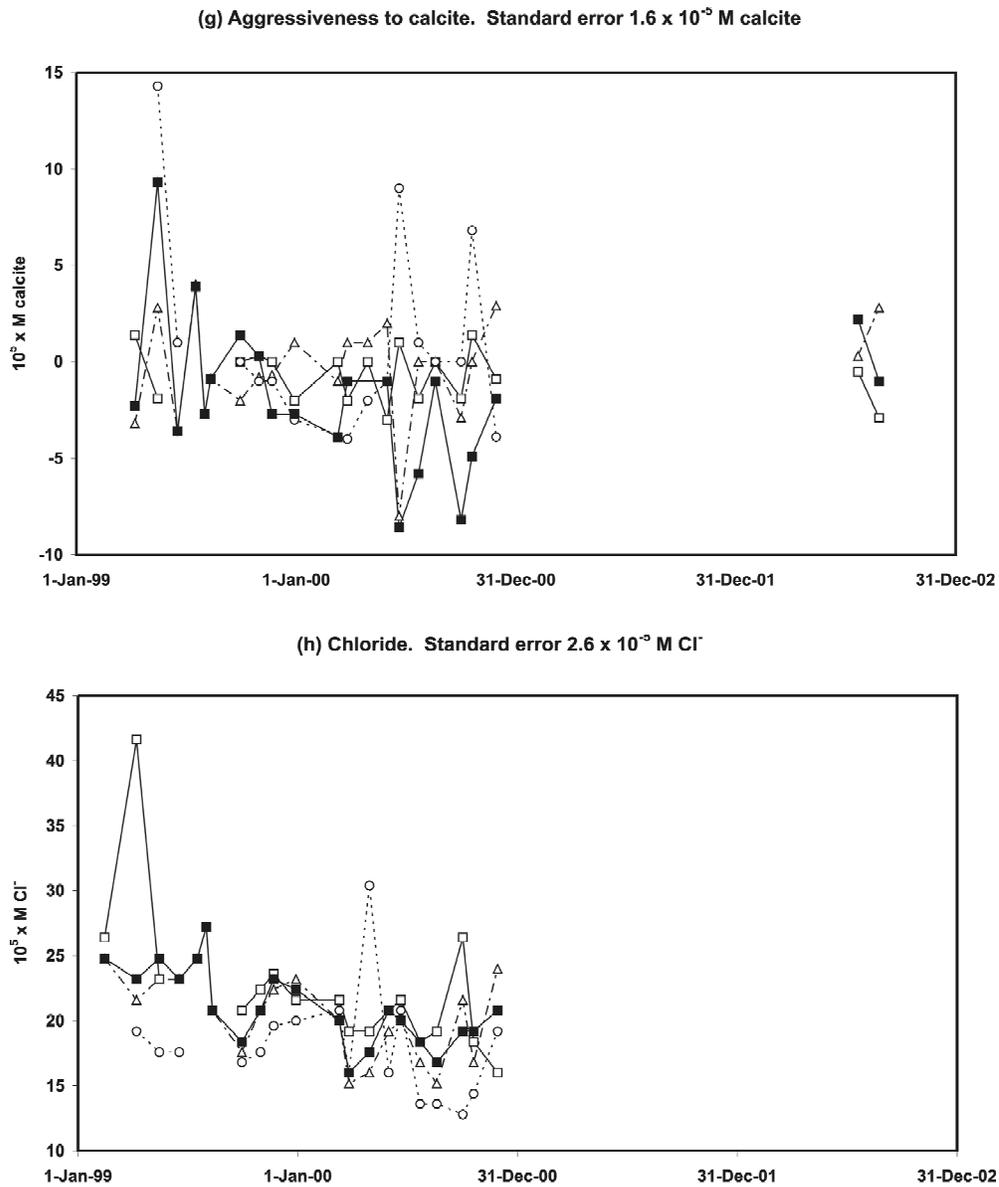
**Figure 5.** (c) Magnesium ( $10^5 \times \text{Molar}$ ) at four sites, from February 1999 to September 2002. (d) Calcium ( $10^5 \times \text{Molar}$ ) at four sites, February 1999 to September 2002.

■ = CI; ○ = Priddy Pool outlet stream; △ = left pipe stream; □ = right pipe stream.



**Figure 5.** (e) Alkaline hardness (ppm as calcite) at four sites, from February 1999 to September 2002. (f) Non-alkaline hardness (ppm as calcite) at four sites, from February 1999 to September 2002.

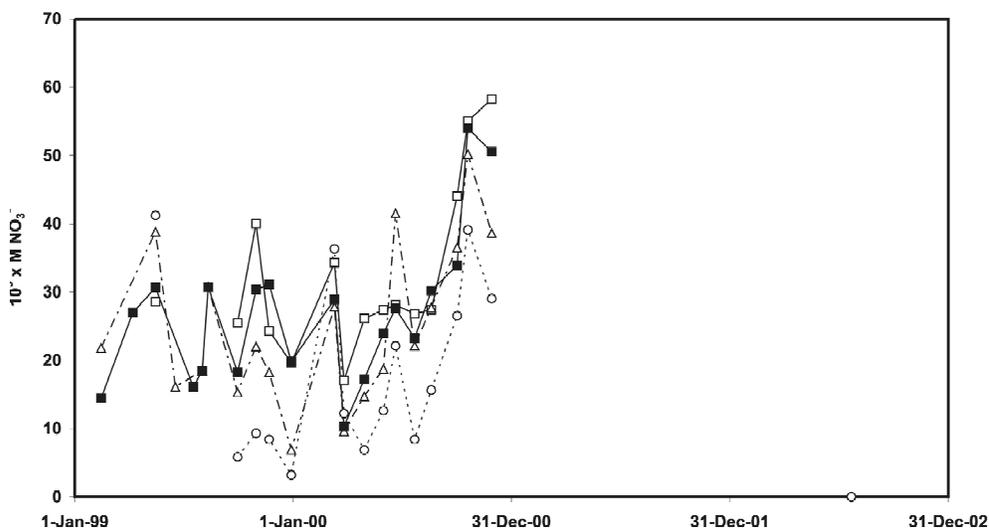
■ = C1; ○ = Priddy Pool outlet stream; △ = left pipe stream; □ = right pipe stream.



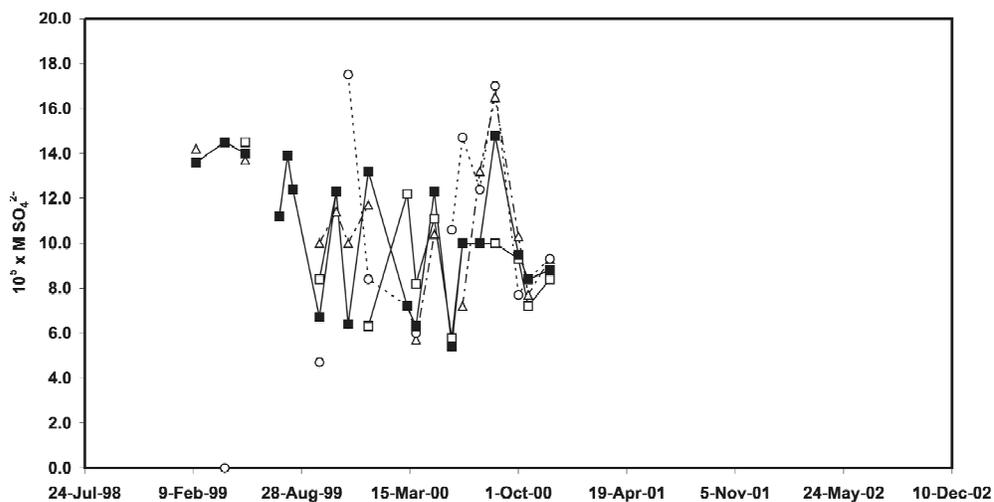
**Figure 5.** (g) Aggressiveness to calcite (ppm as calcite) at four sites. (h) Chloride ( $10^5 \times$  Molar, univalent) at four sites, from February 1999 to September 2002.

■ = CI; ○ = Priddy Pool outlet stream; △ = left pipe stream; □ = right pipe stream.

(i) Nitrate. Standard error  $4.7 \times 10^{-9} \text{ M NO}_3^-$

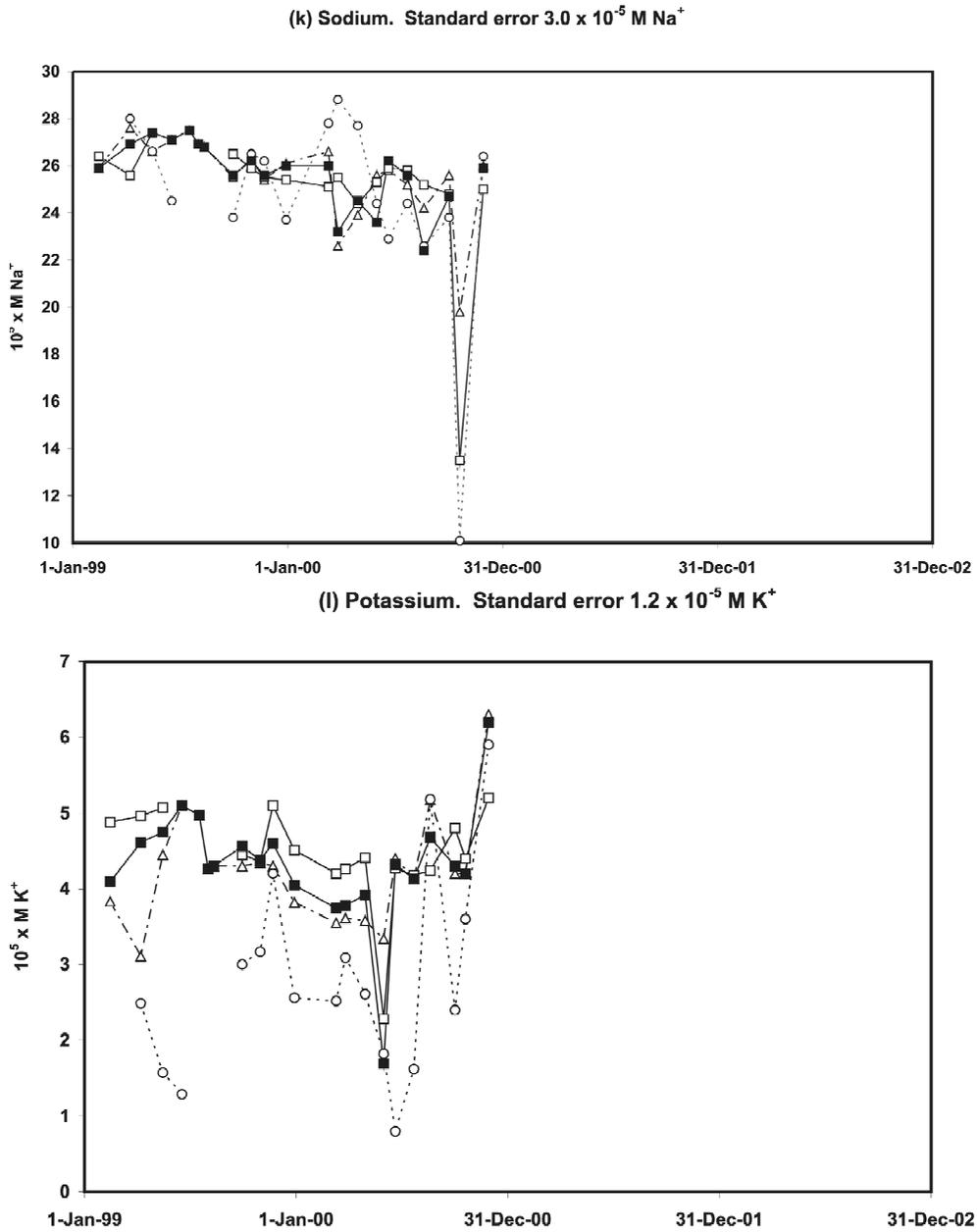


(j) Sulphate. Standard error  $3.1 \times 10^{-5} \text{ M SO}_4^{2-}$



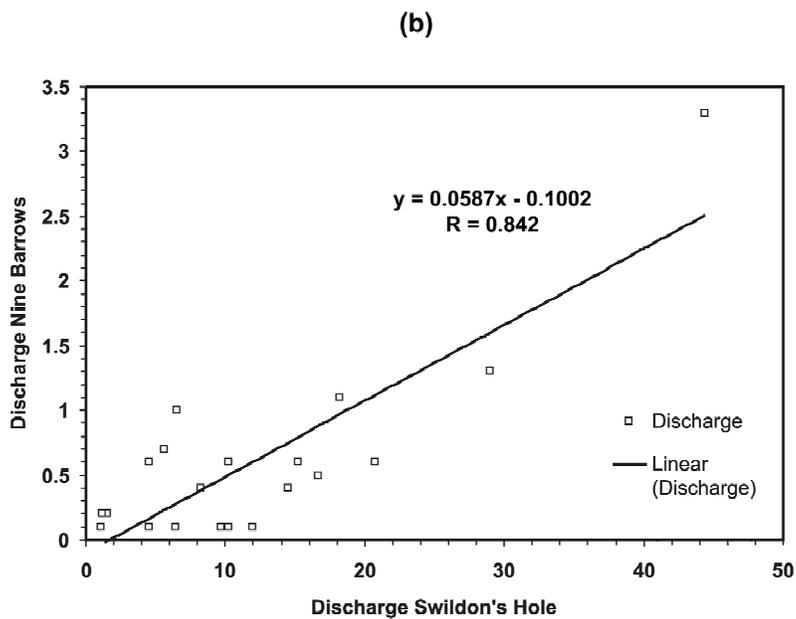
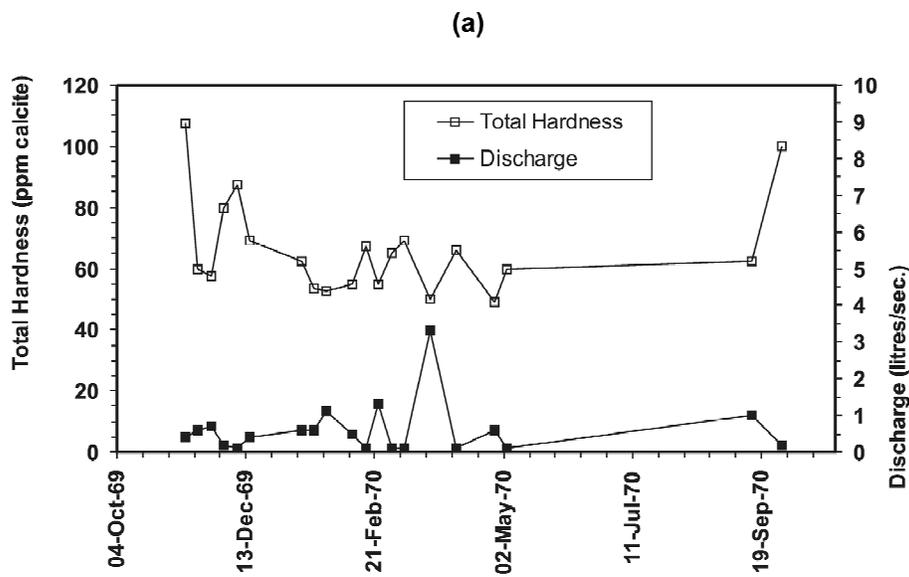
**Figure 5.** (i) Nitrate ( $10^5 \times$  Molar, univalent) at four sites, from February 1999 to September 2002. (j) Sulphate ( $10^5 \times$  Molar, divalent) at four sites, from February 1999 to September 2002.

■ = C1; ○ = Priddy Pool outlet stream; △ = left pipe stream; □ = right pipe stream.

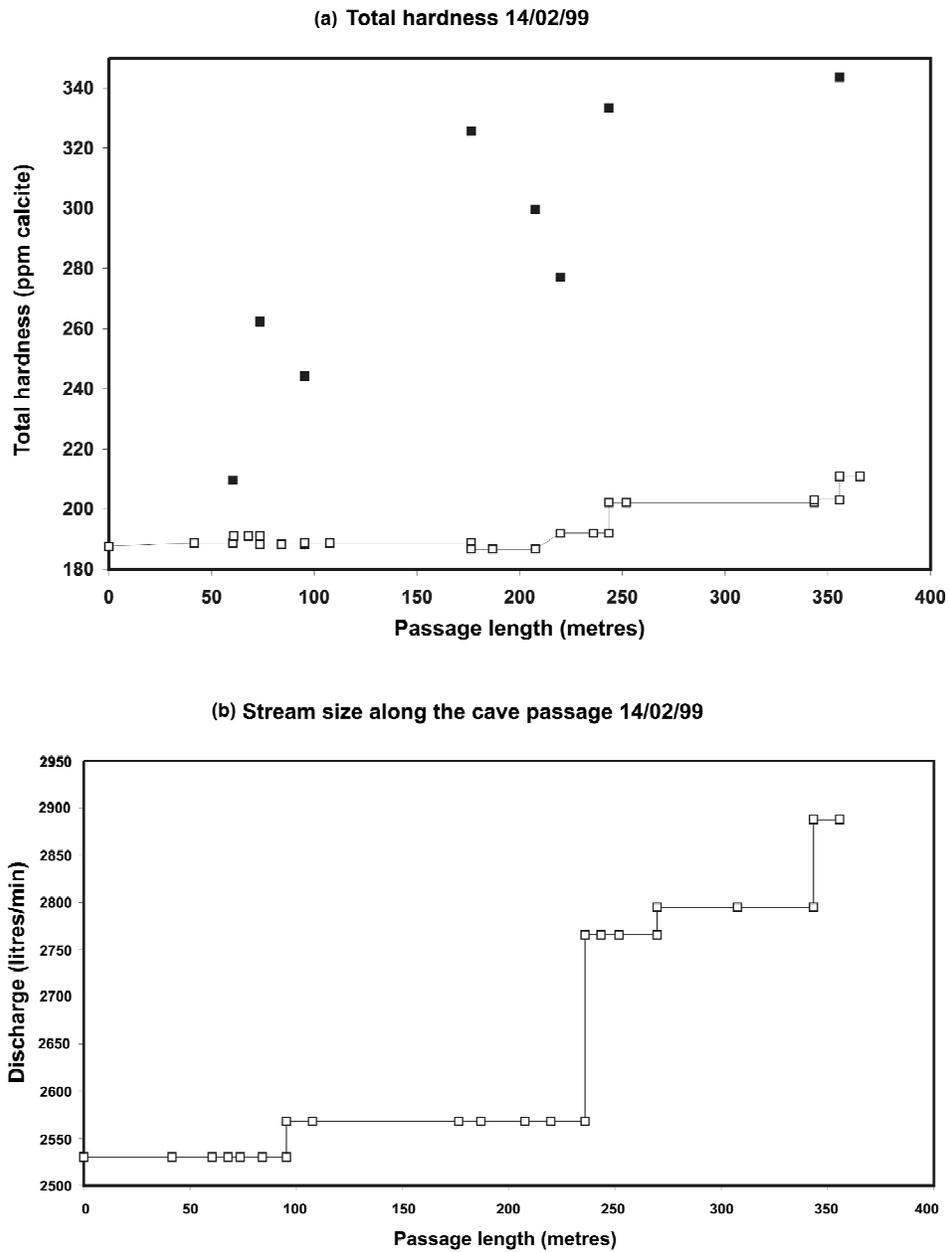


**Figure 5.** (k) Sodium ( $10^5 \times \text{Molar}$ ) at four sites, from February 1999 to September 2002.  
 (l) Potassium ( $10^5 \times \text{Molar}$ ) at four sites, from February 1999 to September 2002.

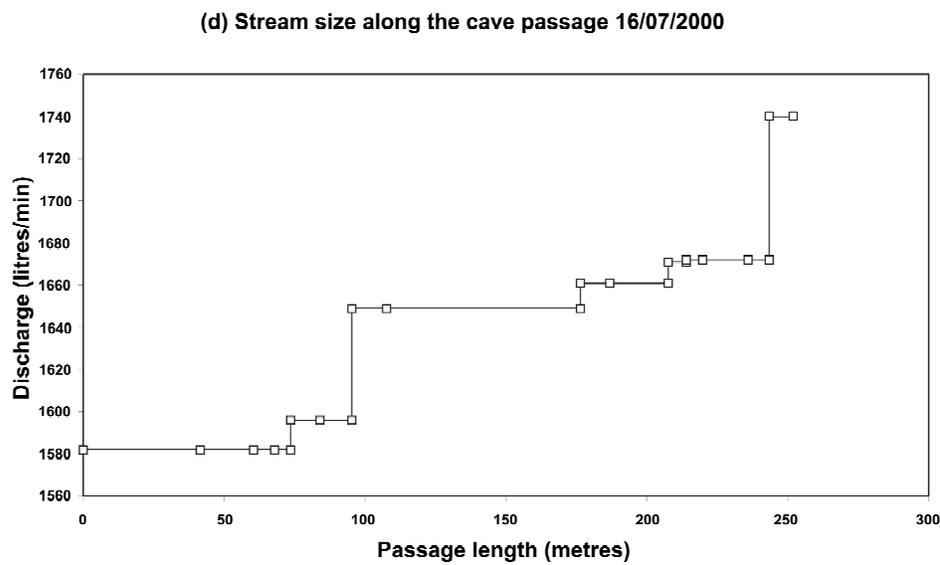
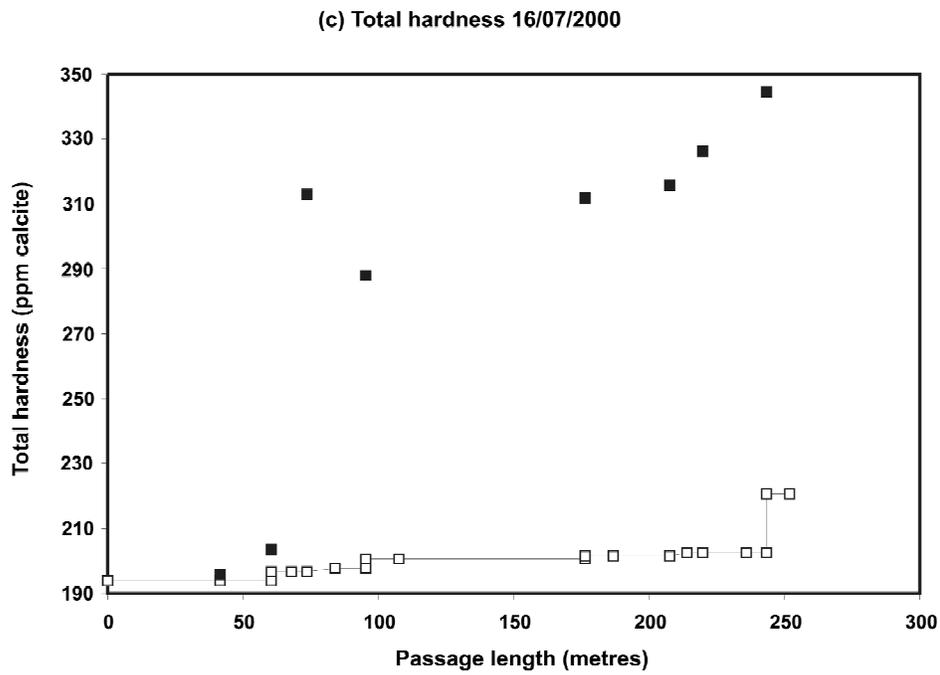
■ = CI; ○ = Priddy Pool outlet stream; △ = left pipe stream; □ = right pipe stream.



**Figure 6.** (a) Total hardness (ppm as calcite) and stream size (litres per minute) at the Nine-barrows Stream at the cave entrance from Nov. 1969 to Sep. 1970. (b) The relationship stream size at Swildon's Hole and that at Nine-barrows Swallet (litres per minute), Nov. 1969 to Sep. 1970. All data by Atkinson.

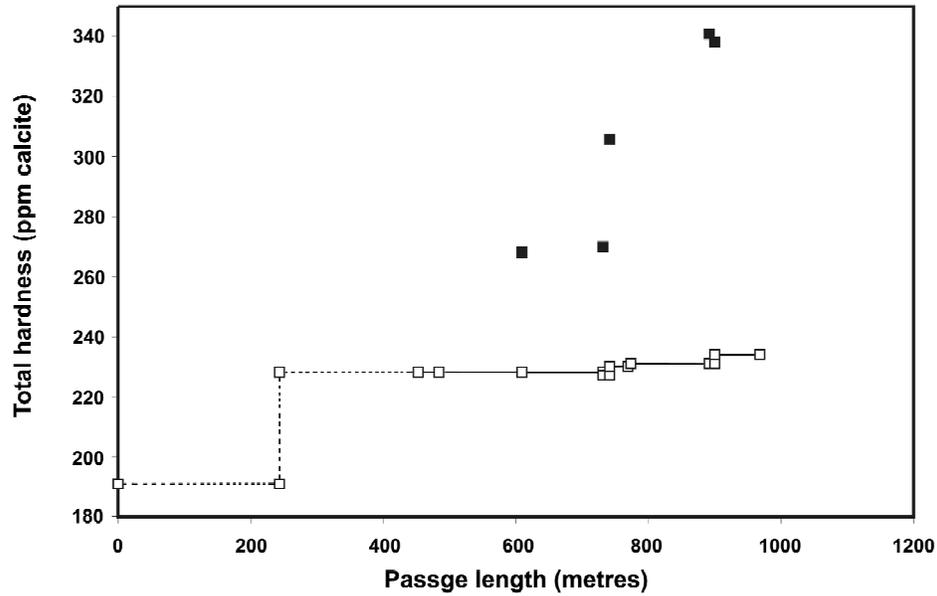


**Figure 7.** (a) The increase in total hardness (ppm as calcite) between the entrance and Sump 3 in Feb. 1999. The total hardness of each inlet is shown. (b) The increase in stream size (in litres per minute) between the entrance and Sump 3 in Feb. 1999.

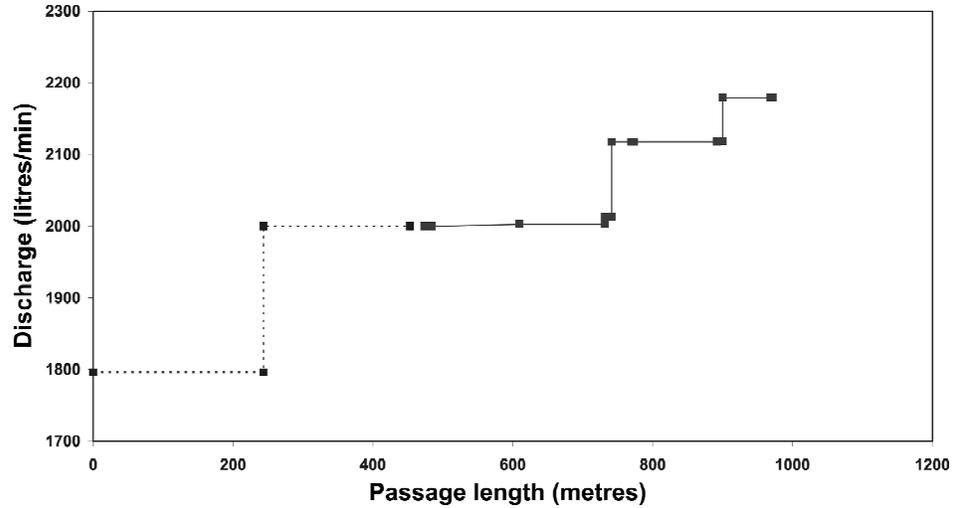


**Figure 7.** (c) The increase in total hardness (ppm as calcite) between the entrance and Sump 3 in Jul. 2000. The total hardness of each inlet is shown. (d) The increase in stream size (in litres per minute) between the entrance and Sump 3 in Jul. 2000.

(e) Total hardness 29/04/2000



(f) Stream size along the cave passage 29/04/2000



**Figure 7.** (e) The increase in total hardness (ppm as calcite) between the entrance and Sump 7 in Apr. 2000. The total hardness of each inlet is shown. (f) The increase in stream size (in litres per minute) between the entrance and Sump 7 in Apr. 2000.

## SUMMARY

1. Compared with the streams sinking in the neighbouring swallet caves, Eastwater Cavern and St. Cuthbert's Swallet, the stream flowing from Priddy Pool has a greater discharge and a much higher total hardness.
2. Water from the borehole 300 m upstream of the swallet has hydrochemical characteristics that are more stable than other surface streams. However, water coming from the Priddy Pool stream is stored within the aquifer in the Lower Limestone Shales, and is consequently a major component of borehole water.
3. Sampling the surface stream in all seasons and a wide range of discharge conditions made it possible to describe the major hydrochemical characteristics of the tributary components of the stream that sinks in Swildon's Hole.
4. Immediately within the cave, the flow of the stream splits into different routes around and through boulders. The various different trickles join together at the head of the Wet Way. During the short distance of the flow of the stream through the boulders, changes of concentrations of dissolved gases (specifically oxygen and carbon dioxide) have been measured previously (Bridge *et al* 1977).
5. Various intermittent trickles in the Old Route in Upper Swildon's and the inlet at Rolling Thunder (at the top of the old 40 ft pot) are shown to have been derived from the surface stream, with a negligible contribution of water from a different source.
6. Hydrochemical characteristics of water at the Rolling Thunder Inlet are much less variable than those of the surface stream from which it is derived. This is the result of carbon dioxide and limestone having dissolved in the intervening space, in an atmosphere with a constant stable concentration of carbon dioxide gas.
7. No inlets beyond the Rolling Thunder inlet are derived from the main stream at the surface.
8. Most of the inlets beyond Rolling Thunder were sampled a considerable distance from the points where they emerged into the cave atmosphere. By the time they reached the sampling points, carbon dioxide in the water had either degassed into the cave atmosphere, or in other conditions extra carbon dioxide had dissolved in the water. Consequently, the variability of the aggressiveness increased, making it more variable than the total hardness. In winter months they had degassed larger quantities of carbon dioxide gas into the cave atmosphere, making the water more strongly supersaturated. But in the summer months, we suggest that the inlet trickles either degassed less carbon dioxide than in winter, or in some cases absorbed more carbon dioxide gas from the cave atmosphere.
9. Although the concentration of carbon dioxide gas in the air in Swildon's Hole varies considerably (Glanville 1993), the atmosphere in the subsoil through which the inlet trickles had travelled must have been much more stable. There could have been only very minor variations in the level of carbon dioxide gas in the intervening space.
10. Seasonal changes in the concentrations of carbon dioxide gas in the air in Swildon's Hole caused the changes in the aggressiveness in the inlets at the sites where the samples were collected.
11. In the inlet trickles beyond Rolling Thunder, variability in total hardness, calcium and alkaline hardness was low. The variabilities of concentrations of nitrate, chloride, sodium and potassium were considerably higher than usual in these inlets.
12. Concentrations of nitrate in 46 out of the 49 samples from the 20 inlet sites beyond Rolling Thunder were very high. In 13 samples with the highest nitrate levels, concentrations of chloride, sodium and potassium were also unusually high. Compared with data from St. Cuthbert's Swallet, Wookey Hole Cave, Gough's Cave and springs and rivers around the

Mendip Hills, many of the present figures for nitrate, chloride, sodium and potassium were surprisingly high. These samples show the chemical signatures that indicate the likely presence of contamination by human or animal waste.

13. The chemical markers noted above are indicative of human or animal waste rather than of contamination by synthetic fertiliser. In some samples such as those from Nine Barrows Hill local drainage streams and intermittent contamination of left and right pipe water, the source was undoubtedly grazing cattle. However, the discovery by Manley and Taylor (1978) of anodic detergents in samples of some inlets deep in the cave suggests that some of the inlets are contaminated by human waste.

14. In normal high water conditions in winter, duplicate samples from all of the 8 inlets between Rolling Thunder and Sump 1 contained high numbers of presumptive *Escherichia coli* bacteria. When the measurements were repeated in low water conditions in summer, two of the inlets were dry, and gut bacteria levels were zero in two more inlets. In the other 4 inlets, gut bacteria remained present in significant numbers even in these most favourable conditions.

15. The poor ion balances found in all the highly polluted samples was a surprising discovery. The suggestion is that, particularly in the most heavily contaminated samples, this problem may have been associated with large organic ions locked into colloidal suspensions, and therefore not available for quantification using the analytical techniques used in the present study. This suggestion is suitable for practical experimentation.

16. There were occasions when the hardness of the surface stream appeared to be "out of phase" with the size of the stream (the sample from 18/11/00 was such an example). There were occasions in the St. Cuthbert's Swallet study when a "misfitting" data-point was obtained, and similar occurrences were reported in streams in the Swansea Valley (Bray, 1975 and pers. comm.). It is suggested that at some time before the stream was sampled, it had been much bigger, and it was likely that the hardness was then considerably lower. This suggestion needs to be investigated, and remote sampling and measuring equipment will be needed in such an investigation.

17. A statistical comparison between the present data and those of Atkinson (1995), made at the same site in 1969 and 1970, showed no difference (at the  $p=95\%$  level). However, the significance of the present regression equation between total hardness and discharge function is lower than in Atkinson's study. In addition, the range of the total hardness figures is lower now than in the data of Atkinson or Ford, when water from the bore-hole was being pumped frequently to provide potable water. The change in the total hardness range, and the poorer regression coefficient, are likely to be a consequence of the decision by Bristol Water plc to stop extracting water from this borehole.

18. Apart from cyclic changes in water temperatures and discharge, there was no evidence of seasonal changes in any solutes in the streams, except aggressiveness in the contaminated inlet streams beyond Rolling Thunder.

19. The stability of many characteristics since Ford's study (1966) and Atkinson's study (1995) is noted. There is no evidence in the present study of characteristics that could be attributed to climatic changes since 1970, although the present data may prove useful in future studies. However, some of the data presented by Ford include figures that are markedly different from the present data. It is possible that Ford collected samples in extremely high water conditions, far higher than in the present studies. This question is important. If this supposition is correct, the implication is that during the trips when Ford collected these samples, water was flowing directly from the surface into the Black Hole Series and the North West Inlet Series, by-passing the normal routes.

## SUGGESTIONS FOR FURTHER RESEARCH

There are a several options for further studies in Swildon's Hole. It would be a good idea to dye trace the Priddy Pool stream and the Nine Barrows local drainage stream (the stream draining the S.W. slopes of North Hill, sinking close to the Bristol Water compound at N.G.R. ST52905165, not the stream sinking at Nine Barrows Swallet), to find out if water from these streams seep into the Black Hole or the North-west Inlet Series streams.

Follow-up studies of some inlet streams will be worthwhile, especially inlet streams in which aggressiveness near their junctions with the main stream have been shown here to have a pronounced seasonal change. It will be productive to sample such an inlet stream from the main stream junction at intervals back to points where they issue from an impenetrable opening in solid rock. Such a study is needed to answer uncertainties concerning the changes in aggressiveness described above. It is important to find out whether aggressiveness shows a similar seasonal change at the points where they issue from solid rock. At the same time, such a study will measure dripstone deposition by these inlet streams and will measure seasonal patterns in this deposition. Other further research possibilities depend on future availability of remote monitoring equipment. This is an area that is currently developing very rapidly.

## ACKNOWLEDGEMENTS

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