

SOME ASPECTS OF THE WATER CHEMISTRY IN THE AREA AROUND MALHAM TARN, NORTH YORKSHIRE

C. WOOF

Freshwater Biological Association, The Ferry House, Ambleside, Cumbria

and E. JACKSON

*Field Studies Council at Malham Tarn Field Centre, Settle, North Yorkshire**

ABSTRACT

Within a five kilometre radius of Malham Tarn Field Centre, lies a wide spectrum of standing and running waters; a strongly acid Pennine Tarn, the highest and largest marl lake in Britain, a variation of alkaline stream types, and a transition from acid to alkaline can be followed in a single stream. This interesting diversity of water chemistry initiated the study. pH, alkalinity, conductivity, calcium, magnesium and total hardness were determined on 65 sites in 9 different water systems over a period of twelve months.

An interpretation of the chemical analyses in relation to the local geology and seasonal variations is presented. The tabulated data provide a useful base for further studies.

INTRODUCTION

THE diversity of landscape features and wildlife habitats found at relatively high altitudes in the area around Malham Tarn is reflected by no less than three separate Site of Special Scientific Interest designations and by a wide range of published material.

Many of the contrasts in rock types, relief and soils that form the basis of this diversity have an important effect on the chemistry of running and standing waters, which in turn are wildlife habitats in their own right. This paper provides data on some of the spatial and seasonal variations in water chemistry throughout the area, particularly for those waters often studied by groups and individuals visiting Malham Tarn Field Centre.

A series of standing water sites and running water systems were investigated over a 12 month period and are described using some of the more commonly encountered chemical characteristics. An opportunity is also taken to present a variety of previously unpublished data from other sources. It is hoped that these results will provide a useful basis for more detailed chemical, ecological or geographical studies. One of us (C.W.) concentrated on the chemical analyses and interpretations; the other (E.J.) provided information to put these in their appropriate local context.

PHYSICAL BACKGROUND

Malham Tarn lies at 375 m in the centre of Malham Moor, an area of high ground at the head of Airedale in the Yorkshire Dales (Figure 1). To the south of the Tarn, the land rises gently for about 2 km, dissected by several south-facing valleys, then drops sharply away

*Present Address: Field Studies Council at Flatford Mill Field Centre, East Bergholt, Colchester, Essex.

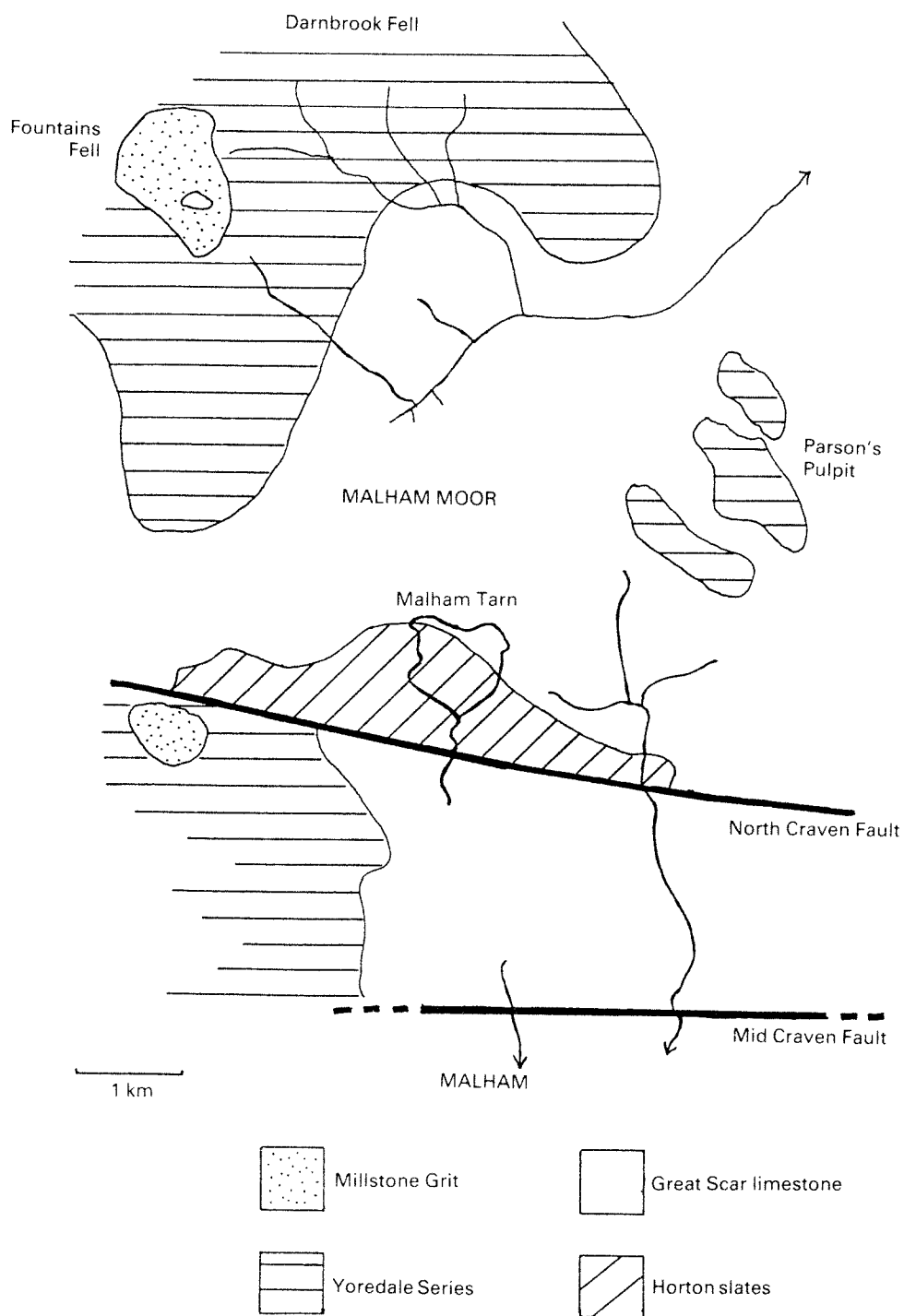


FIG. 1.

The area around Malham Tarn.

from 390 m to around 200 m at Malham village. To the northeast, the land rises more steeply for 3 km to Parson's Pulpit at 538 m. This area is separated by the broad valley of Cowside from Darnbrook Fell and Fountains Fell, which lie to the northwest of the Tarn at 624 m and 668 m respectively.

The whole area is underlain by Silurian Slates of the Horton Formation. These provide an impermeable basement of inert, base-deficient rocks, although they form the surface geology only in the vicinity of the Tarn. Around this inlier, Lower Carboniferous Great Scar limestone is dominant. This rock mass is up to 200 m thick and consists of extremely pure crystalline limestones, 94–99% of which are comprised of calcium carbonate and the remaining percent being mainly magnesium carbonate. In marked contrast to the slates, the limestone has very high permeability due to the widening by dissolution of well developed, near horizontal, bedding planes and vertical joints.

On the higher ground to the northwest of the Tarn, and to a small extent to the northeast, the limestone is succeeded by the Yoredale Series. This consists of repeated sequences of limestone, shale sandstone and, occasionally, coal, with depths varying from a few centimetres for the coals up to tens of metres for the other facies. The limestones are generally darker and less pure than those in the Great Scar formation, but still retain a high permeability. On the steep slopes of Fountains and Darnbrook Fells, the Yoredales reach a depth of almost 200 m. On the summit of Fountains, the dominance of acidic rocks is restored. Here Yoredales are overlain by the Millstone Grit formation, represented by 30–40 m of coarse and fine grained sandstones with occasional thin shale and coal bands.

Earth movements along the Craven Fault zone, and the effects of the Pleistocene glaciations, both help to explain further the variation in rocks and relief. The steep limestone slopes to the north of Malham village form a scarp linked to early Carboniferous movements along the Mid Craven fault. There has been little retreat from this fault line: the scarp was buried under late Carboniferous sediments and has only been exposed more recently. Post-Carboniferous movements along the North Craven fault created another limestone scarp, associated with a downthrow of about 100 m to the south. This scarp has subsequently retreated northwards, locally between 1 and 2 km, so bringing the Horton slates close to the surface. Glacial erosion in the last (Devensian) glaciation contributed to this process, scouring the limestone and slates to define the shallow basin in which Malham Tarn and its associated wetlands now lie. Fountains Fell Tarn lies on the summit plateau in a basin of similar origin. Glacial and meltwater erosion also played an important part in modifying existing valleys and creating new ones, helping to determine the postglacial drainage patterns. Drift deposits of glacial and meltwater origin have also affected the drainage by masking the solid rock in many places, particularly to the east and west of the Tarn and on the slopes between Fountains and Darnbrook Fells.

Soil development in early postglacial times produced, predominantly, a pattern of rendzinas on limestones and brown earths on drift and other rock types. These soils supported a little-altered climax forest until the arrival of Neolithic farmers around 5000 years ago. The progressive removal of the forest cover to provide grasslands for cultivation and grazing, coupled with the onset of the wetter, cooler conditions of the sub-Atlantic in the last 3000 years, initiated the acidification of the soils, leading to podzolisation over some of the deeper drifts. On the ground to the northwest, with the highest rainfall, this has been matched by the development of an extensive cover of deep blanket peat.

Under the thinner limestone and drift soils, limestone dissolution has been an important associated process; widening joints and so creating subsurface routes for water throughout the limestone rock mass. The process is even more obvious in the stream channels that do

run over limestone: many have sinks that remove varying amounts of the surface water depending on the antecedent conditions, often leaving the lower reaches of the channel dry. Further discussion of soil forming processes may be found in Trudgill (1985).

Throughout the postglacial within the Tarn basin, wetland development has been a dominant process. The early postglacial water level was most likely higher than at present, with an outflow to the east via Gordale. With the cutting of an alternative outflow to the south, water levels fell, allowing calcareous mire to develop on the exposed ground to the east of the Tarn. In the shallowest water to the west of the Tarn full hydrosere development has taken place, from swamp through fen to raised bog, the depth of present peat being commonly at least 5 m. As these wetlands developed, surface water was confined as small streams flowing into the Tarn, mainly from the north and west margins. These have associated Zones of swamp and fen alongside them. Further details of the geology and landforms, soils and present vegetation patterns may be found in Shaw (1982), Clayton (1981) and Sinker (1960).

THE STUDY AREA

In attempting a broad characterisation of the water chemistry it was found convenient to divide the water bodies into two main groups.

The Standing Water sites, shown on Figure 2, which consist of:

- *Groups of ponds in the wetland complex known as Tarn Fen and Tarn Moss.
- *Malham Tarn and Fountains Fell Tarn.

The Running Water systems, shown on Figure 3, which are divided into four catchments:

- *Darnbrook Beck—down to its confluence with Cowside Beck.
- *Cowside Beck—down to just below the confluence with Darnbrook Beck.
- *Gordale Beck—down to Gordale bridge.
- *Malham Tarn—the main inflow streams and the outflow stream, down to Water Sinks.

The catchment boundaries are based on the surface relief, but they should be treated with caution where they cross the Great Scar limestone. The dominance of subsurface flows through this rock mass raises the possibility of leakage from one catchment to another. This is most likely from the Tarn and Gordale catchments into the Cowside catchment, following the regional dip in the limestone of 5° to the NNW.

COLLECTION AND TREATMENT OF SAMPLES

At each site, the water was collected in a 300 ml wide-mouthed polyethylene bottle which, wherever possible, was filled by complete immersion just beneath the surface and the top screwed down under water to exclude air from the sample (Golterman *et al.*, 1978). After collection, precautions were taken in the field to keep the samples cool and dark. The Standing Water samples were collected on three occasions: August 1980, April 1981 and August 1981. The Running Water samples were collected on seven occasions between July 1980 and June 1981.

The samples were analysed at the Freshwater Biological Association laboratories, Windermere. pH, conductivity and total alkalinity were usually determined the day after collection having allowed the water samples to reach equilibrium with room temperature. The calcium and magnesium analyses were carried out at a later date after acidification of samples with a Lanthanum/Hydrochloric acid solution, this reduces the interferences caused by refractory compounds formed during the analytical procedure (SCA, 1979).

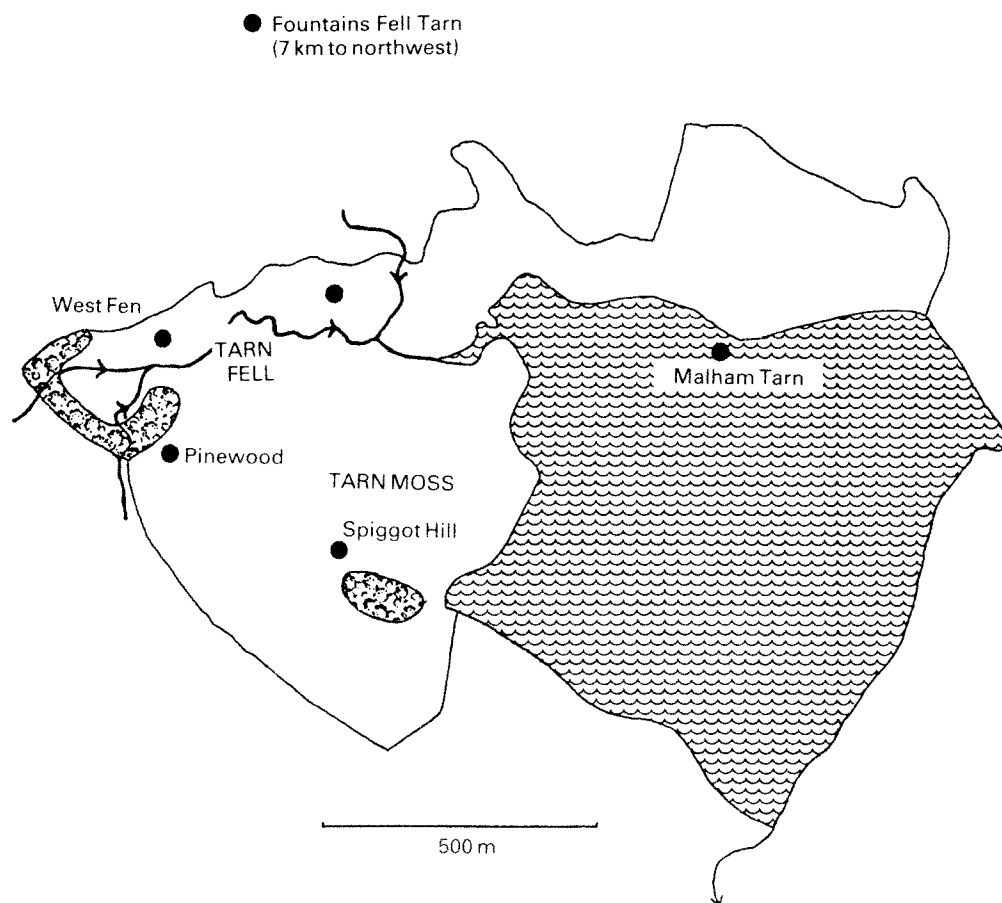


FIG. 2.
Standing water sites.

Determinands

pH

pH was measured on a Radiometer pH meter with glass electrode and referenced to pH 4.0 and pH 8.0 standard buffer solutions. The sample was slowly stirred with a magnetic stirrer and the pH noted after 2–3 minutes.

The pH of a solution is a measure of its acidity (Stumm & Morgan, 1981). The more acid the solution the lower is the value of pH, pH7 being neutral.

pH is widely used by limnologists to show the general chemical characteristics of a water and is a parameter in the free carbon dioxide/alkalinity/pH relationship (Mackereth *et al.*, 1978). The majority of natural waters has a pH ranging between 4.0 and 9.0. Most are slightly alkaline due to the presence of bicarbonate and carbonate. Gaseous inorganic carbon, carbon dioxide, which is a weak acid, can dissolve in water and affect pH. During photosynthesis, aquatic plants use dissolved carbon dioxide for carbon fixation. In poorly buffered waters, i.e. waters with a low alkalinity, photosynthesis can reduce the carbon dioxide content and lead to large increases in pH during daylight hours.

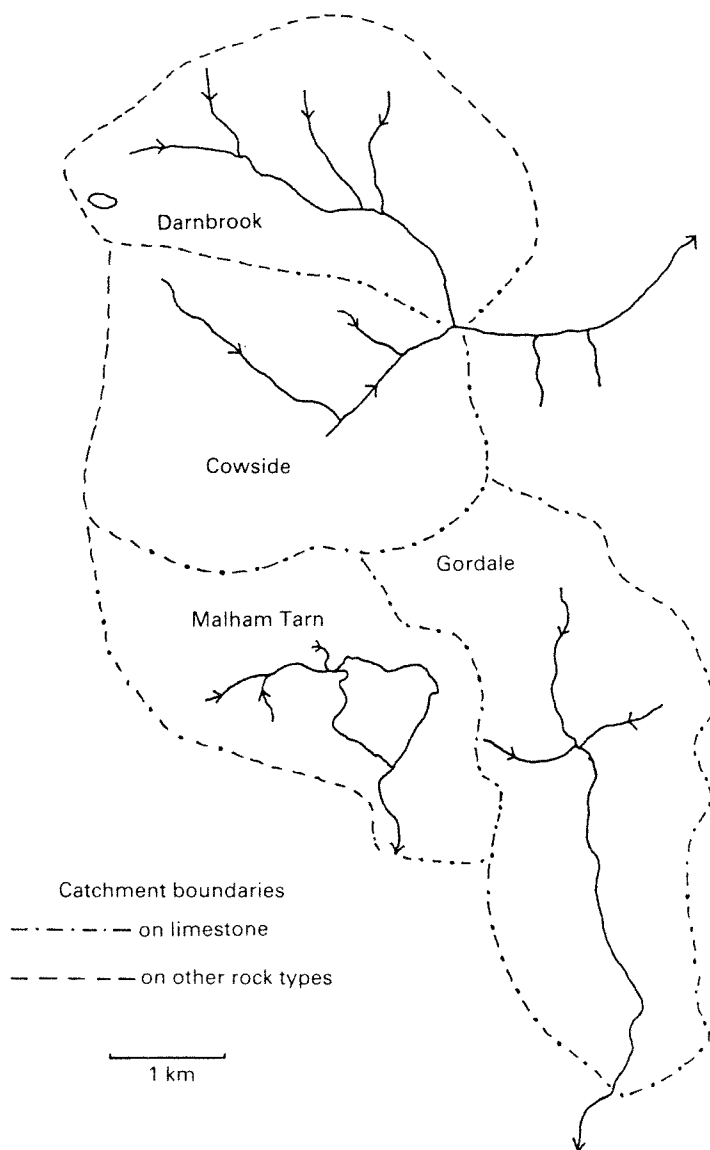


FIG. 3.
Running water systems.

Conductivity

A Christison PTI-18 Digital Conductivity meter was used for these measurements. The readings were referenced to 25°C using 0.001 M KCl as the calibration solution (SCA, 1978).

The electrical conductivity of a water depends on its concentration of dissolved salts and a relationship can be expected between conductivity and the total ionic concentration. Values are expressed in microsiemens per centimetre ($\mu\text{S cm}^{-1}$), which is equivalent to micromhos per cm ($\mu\text{mho cm}^{-1}$). It should be noted that conductivity varies with temperature, so it is important to state the temperature at which the measurements were taken.

In waters below pH 4.5 and above 9.5, H^+ and OH^- ions make a significant contribution to conductivity values. Corrections can be made for the conductivity attributable to these ions and the results are then termed corrected or reduced conductivity (Golterman *et al.*, 1978). Because of this effect, it is normal to include a pH measurement along with the conductivity value.

Total Alkalinity

This was measured using an electrometric titration (DOE, 1972). A Radiometer pH meter with glass electrode was used and the sample titrated with 0.02 M HCl to an end point at pH 4.5.

Alkalinity is a measure of the concentration of weak acid salts. In most natural waters these are mainly bicarbonates, and sometimes carbonates. In the determination, which is carried out by titration with standard acid, the carbonates are neutralised around pH 8.3 and the bicarbonates at pH 4.5. In this study alkalinity is referred to as Total Alkalinity ($HCO_3^- + CO_3^{2-}$) and expressed in $mg\ l^{-1}\ CaCO_3$. Alkalinity values can also be expressed in milliequivalents per litre: $1\ meq\ l^{-1}\ HCO_3^- = 50\ mg\ l^{-1}\ CaCO_3$.

Calcium, Magnesium and Total Hardness

The acidified samples were analysed for calcium and magnesium by aspiration into an air/acetylene flame on a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer, using operating conditions recommended in the Perkin-Elmer manual.

Total hardness was calculated from the results of the calcium and magnesium determinations using the equation (APHA, 1985):

$$\text{Hardness, mg equivalent } CaCO_3\ l^{-1} = 2.497 [Ca, mg\ l^{-1}] + 4.118 [Mg, mg\ l^{-1}]$$

The total hardness of a water is briefly defined as the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate, in milligrammes per litre (APHA, 1985). This can be determined either by calculation, as above, or by an EDTA titration method (SCA, 1981; Douglas, 1968). Several metal ions, however, can interfere with the EDTA procedure. In sufficient concentrations, aluminium, copper, iron, lead, manganese and zinc either titrate as total hardness, giving an exaggerated value, or cause indistinct end-points. These interferences can be reduced by the addition of suitable indicators (APHA, 1985; SCA, 1981).

In the Malham area, such interferences are most likely in water from two main sources. Acid moorland waters (Morris *et al.*, 1979), such as those from the upper reaches of Darnbrook Beck, may contain aluminium, iron and manganese. Waters from areas such as High Mark near Parson's Pulpit, where there are abandoned mine workings and spoil heaps, may contain copper, lead and zinc. Precautions should be taken accordingly if EDTA titrations are used for total hardness in these cases.

Additional analyses

Sodium and potassium were determined by atomic absorption spectrophotometry. Anions (largely sulphate, chloride and nitrate) were measured by an ion exchange method (Mackereth *et al.*, 1978).

Precision data for analytical methods

In order to demonstrate the degree of precision of the various analytical methods used, 10 replicated determinations were carried out on one day. The results are shown in Table 1. The calcium and magnesium measurements were performed on synthetic solutions, while for conductivity and total alkalinity real samples were used.

Table 1. *Precision data for analytical methods*

Determinand	Concentration	Precision, as the coefficient of variation
Conductivity	59 $\mu\text{S cm}^{-1}$	0.9%
	460 $\mu\text{S cm}^{-1}$	0.4%
Total Alkalinity	7.8 $\text{mg l}^{-1} \text{CaCO}_3$	5.0%
	180 $\text{mg l}^{-1} \text{CaCO}_3$	0.7%
Calcium	0.10 mg l^{-1}	27%
	4.0 mg l^{-1}	0.8%
Magnesium	0.01 mg l^{-1}	16%
	0.5 mg l^{-1}	1.9%

$\mu\text{S cm}^{-1}$ = microsiemens per centimetre. mg l^{-1} = milligrammes per litre.

THE STANDING WATER SITES

The results for the Standing Water sites are given in Appendix 1. Descriptions of each site and the factors influencing their water chemistry are linked to a discussion of the main characteristics and trends shown in the results. Seasonal variations in the determinands throughout all the Standing Water sites are also considered.

The Wetland Ponds

These ponds lie in the complex mosaic of wetlands on the west side of Malham Tarn. The present pattern of wetland types, consisting predominantly of surface vegetation communities over deep accumulations of peat, reflects important differences in hydrological conditions.

Wetland areas which are still flushed by mineral-rich soilwater and groundwater, either alongside the streams or at the base of the surrounding slopes, develop under "soligenous" conditions. Open water fringes, supporting swamp communities over organic-rich muds, grade into firmer ground characterised by fen communities over accumulations of circumneutral or alkaline fen peat.

Soligenous conditions were once dominant throughout, but as peat accumulation from fen vegetation caused the wetland surface to rise, those areas furthest from the direct influence of groundwater came increasingly under the influence of mineral-poor rainwater only. In these "ombrogenous" conditions, communities of acid-tolerant bog vegetation replaced the fen communities, leading to the accumulation of acid "raised bog" peat. The present gradient between soligenous and ombrogenous conditions is therefore particularly important since it reflects changes in water chemistry as well as hydrology.

Conventionally, the wetland is split into two main parts. The area between the northern edge of the wetland and the main inflow streams, where the mosaic of swamp, fen and raised bog is most complex, is known as "Tarn Fen". This in turn is split into the West Fen, Mid Fen and East Fen. The larger area to the south of the inflow stream dominated by raised bog is known as "Tarn Moss".

Throughout Tarn Fen and Tarn Moss there are groups of small and medium-sized ponds and ditches cut into the peat. Some are old features, but many have been deliberately created over a thirteen year period since 1971 to diversify the freshwater habitats. These also provide replicate sampling sites for freshwater studies, so minimising disturbance to

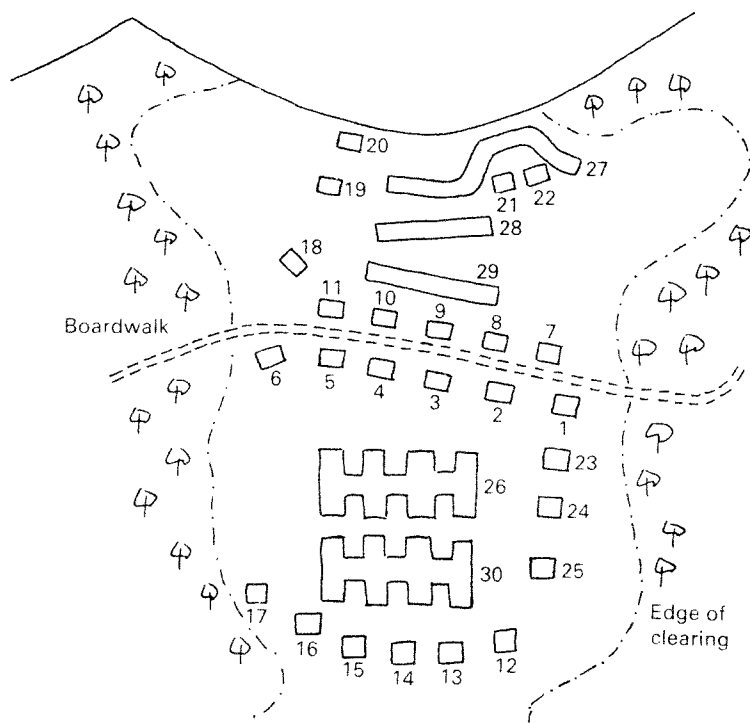


FIG. 4.
Mid Fen ponds.

those ponds established for a longer period. The four groups of ponds most frequently used by students visiting the Field Centre were investigated, although not every pond was sampled because of limitations on analysis time. The general location of the ponds is shown on Figure 2; and a more detailed plan is given at the start of each section below. The opportunity is taken here to standardise the numbering system for all these ponds, and each is marked accordingly on the ground.

Mid Fen

The largest series of ponds has been excavated within the Mid Fen, an area zoned primarily for student use (Disney, 1975). The sequence of excavation was as follows (Figure 4):

1971 Ponds 1 to 11

1972 Ponds 12 to 17

1973 Ponds 18 to 22

(Four more were dug at this time but have since been joined to form Pond 27.)

1974 Ponds 23 to 25

1976 Pond 26

1977 (One pond was dug on the northern margin but has since been incorporated into Pond 27.)

1978 Pond 27, linking the five mentioned above; Ponds 28 and 29

1984 Pond 30

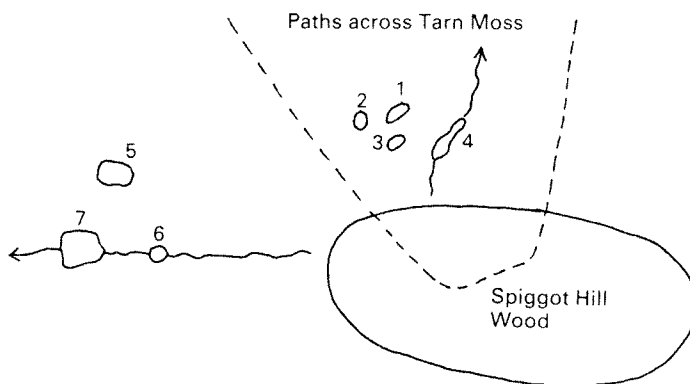


FIG. 5.
Spiggot Hill ponds.

The close relationship between water chemistry, hydrological conditions and wetland types is well illustrated by the range of values obtained from the Mid Fen ponds, where chemical characteristics change markedly over relatively short distances.

Ponds 27 and 28 lie on the northern margin of the Mid Fen. They consistently have the highest pH values, in the range 5.3 to 7.3; the highest calcium values between 4.5 and 37 mg l⁻¹; and the other determinands also normally high. This underlines the predominance of soligenous conditions, with mineral-rich water draining from the drift mounds behind. These in turn are reflected by the surrounding communities of fen vegetation. Although not sampled, ponds 19–22 alongside 27 and 28, might be expected to share similar characteristics.

Most of the ponds, however, are cut in the centre of the peat dome. 1–6, 12 and 23–26 are on the south side of the board walk; 7–11, 18 and 29 on the north side. Most have low pH values in the range 4.1 to 5.3; low calcium concentrations in the range 1.0 to 4.0 mg l⁻¹ and low values for the other determinands. These ponds are, therefore, cut into acid peat, now dominated by ombrogenous conditions. The chemical gradient through ponds 27, 28, 29 and 8 is a good reflection of the changes in hydrological conditions.

Spiggot Hill

Most of the ponds here are old-established features (Figure 5), possibly related to early peat cutting, but are difficult to date, ponds 1–3 lie about 40 m from the northern edge of the drift mound that forms Spiggot Hill; they are only a few metres across and 0.5 to 1 m deep. Pond 4, just to the east of this group, is more elongated and is part of a drainage channel extending northwards, that is well marked out by differences in vegetation. Pond 5 is a larger feature, 8 × 8 m, in an area of dead ground 150 m to the northwest of the hill. Ponds 6 and 7 lie 100 and 150 m respectively along the drainage channel extending westwards from the hill. Pond 7 was enlarged and dammed to 12 × 12 m in 1981. Ponds 5, 6 and 7, however, were not sampled on this occasion.

Ponds 1, 2 and 3 all have similar chemical characteristics to those cut into the acid peat on the Mid Fen. They have low conductivities, with pH values in the range 3.9 to 5.3. In fact, ponds 2 and 3 are the only locations, apart from Fountains Fell Tarn, where the pH falls below 4.0. Of the other determinands, calcium appears to be particularly low. A clear contrast with the ombrogenous conditions around these three ponds is seen in pond 4.

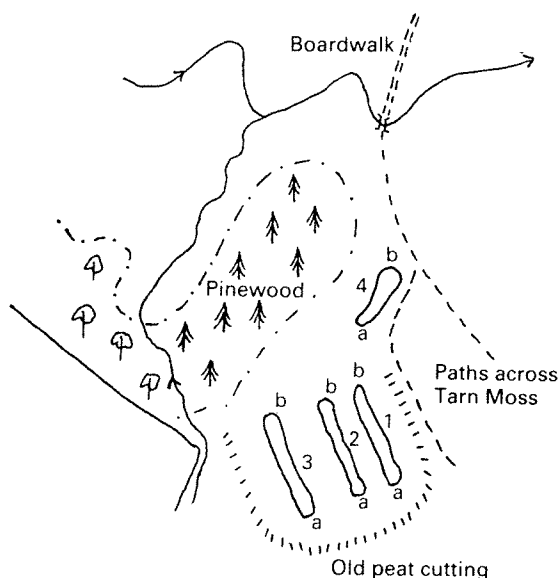


FIG. 6.
Pinewood ponds.

Here all the determinands are markedly higher, a reflection of the mineral status of the water draining from the limestone-rich drift mound of Spiggot Hill.

Pinewood

All the ponds here have been created recently (Figure 6); 1, 2 and 3 are ditches 30 m long and 1–3 m wide lying within an older peat cutting to the southeast of the Pinewood, which is the southern arm of Horseshoe Wood. Pond 4 is 17 m \times 2–3 m and lies in an area of unexploited peat to the north of the main cutting. The sequence of excavation was as follows:

- 1977 Pond 1
- 1978 Pond 2 (part)
- 1979 Pond 2 (completed); Pond 3
- 1980 Pond 4

Since these ponds are more extensive than most, samples were taken from both ends: e.g. 3a and 3b.

Of the ponds in the cutting, 3 on the southwest side has values for pH and alkalinity consistently higher than the other two. Ponds 1 and 2 are more closely matched: in August 1980 and April 1981 most determinands are slightly higher in pond 1, but in August 1981 the position is reversed; so there are no obvious chemical gradients through the ponds that might reflect their position in the cutting.

If the values at either end of the ponds are considered, pond 3 is once again the more consistent: the northwest end, 3b, usually has the higher values. In ponds 1 and 2 conductivities at either end are virtually identical, but there appears to be a seasonal swing in pH and alkalinity with the northwest ends having slightly higher values in autumn and the southeast ends in spring.

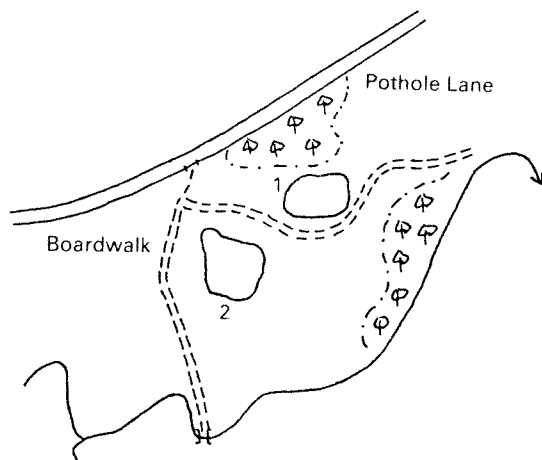


FIG. 7.
West Fen ponds.

Pond 4 should be considered on its own because of its location. Values for all determinands tend to be higher than in the other three ponds and are always so at the shallower southern end, 4a. The northern end was deliberately excavated deeper, but, unexpectedly, part of a mound of limestone-rich drift was exposed at the shallower end. This accounts for the internal variations and also for its values being higher than the other three ponds, despite being cut into acid bog peat.

West Fen

There are two old-established ponds here (Figure 7). Although the exact details are unclear their history may be as follows:

- c. 1820 Two ponds were excavated in the West Fen to contain newly hatched trout. The remnants of acid bog peat around the present ponds suggest that the area had been fairly extensively exploited for peat prior to this.
- c. 1880 The ponds were abandoned in favour of new ones on the Cowbeck (North Inflow).
Colonisation of the open water occurred unchecked until the mid 1960's. Pond 1 has since been periodically cleared, but the vegetation in pond 2 has remained largely undisturbed.
- 1964 Sedge swamp in pond 1 cleared completely.
- 1975 One fifth of the area of pond 1 has been cleared in alternate years since this date to re-establish part of the open water habitat and to demonstrate the recolonisation process.

Both ponds have high pH values in the range of 6.6 to 7.5 and consistently high values for the other determinands. This reflects soligenous conditions: the ponds are flushed by mineral rich groundwater from the slopes to the north and are colonised by swamp and fen communities. Pond 2 has the highest conductivities, alkalinities, calcium and hardness values of all the standing water sites sampled.

Malham Tarn and Fountains Fell Tarn

Malham Tarn covers 62 hectares and though typically 2–3 m deep, is over 4 m in a few places. With the exception of several small streams draining from the eastern edge of Tarn

Moss, all the groundwater entering the Tarn is derived from limestone or limestone-rich drift.

Fountains Fell Tarn covers only 2 hectares and is no more than 0.5 m deep. The input of groundwater here comes from blanket bog peat developed over coarse sandstones. Unlike Malham Tarn, Fountains has no permanent outflow. The input of water is roughly matched by evaporation and slow percolation to springs near the base of the Millstone Grit formation.

In general, these two larger water bodies are at opposite extremes of the chemical spectrum found throughout the Standing Water sites. Fountains Tarn recorded the lowest pH values and some of the lowest values for the other determinands. Its chemistry is therefore extremely base-deficient. This, combined with severe conditions in winter, when it experiences prolonged freezing, makes it the poorest body of permanent standing water in the study area.

By contrast, Malham Tarn recorded some of the highest values for all the determinands making it extremely base-rich for an upland lake. Since it can also be viewed as part of a running water system, further comments are made in the appropriate section below.

Seasonal variations in the determinands

Most of the Wetland ponds showed minimum calcium, magnesium and total hardness values for the April sampling date. This most likely reflects dilution due to snowmelt and high antecedent rainfall. Lower rainfall and higher evaporation in the summer months gave higher concentrations for these determinands on both dates.

These changes help to increase the pH values in autumn as well. In some of the waters which take their drainage from the acid peat, however, a depression in pH was observed. This may be due to rainfall immediately before sampling flushing out organic acids that had been accumulating in the peat. In the other ponds this effect is neutralised by the mineral-rich soil water.

Detailed comments on the conductivity trends within the ponds are not really appropriate, since in many cases the pH falls below 5.0. Conductivities are then affected by high concentrations of H^+ ions, which tend to mask the effect of other ions.

THE RUNNING WATER SYSTEMS

The results from the Running Water systems are given separately for each of the determinands in Appendices 2–7.

Darnbrook

Darnbrook Beck has the greatest surface water drainage area of the systems investigated (Figure 8). A large part of the catchment is on the superficial drift which masks the relatively impermeable Yoredale and Millstone Grit Formations, although the streams do expose the solid rock in many places.

Results from the eight sampling sites show this system as an excellent example of the way variations in stream water chemistry broadly reflect lithological changes.

The western headwaters of Darnbrook Beck rise at a series of springs near the base of the Millstone Grit Formation, well within the overlying cover of blanket peat on Fountains Fell. At the headwater sites 1 and 2, the water has moved a short distance onto the uppermost Yoredale shale. Percolation of water through the surrounding inert rocks and

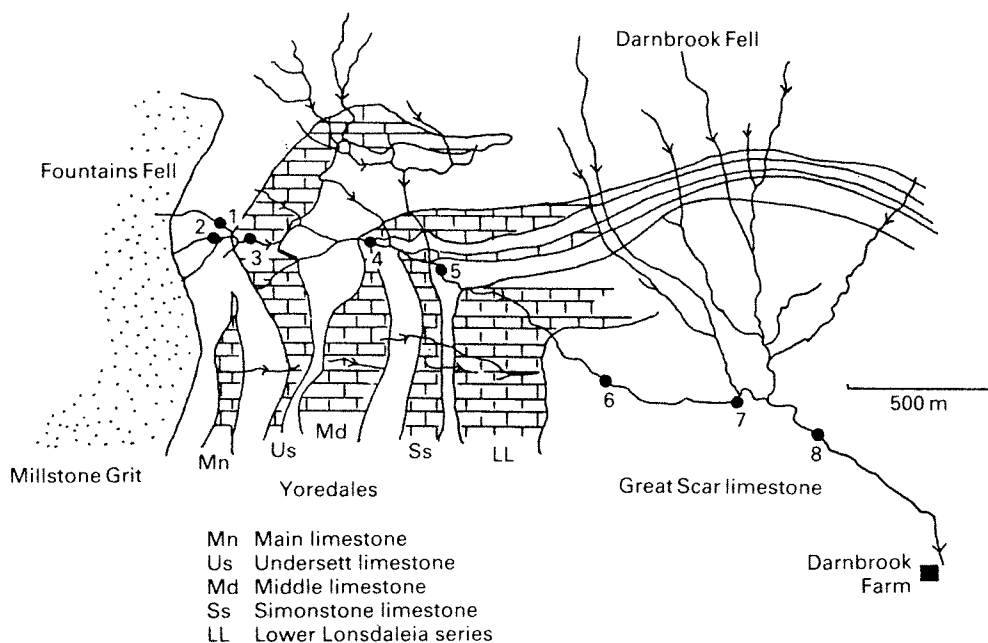


FIG. 8.
Darnbrook.

acid soils is reflected by the very low values for all determinands at these sites, with alkalinity virtually non-existent.

Site 3 lies 50 m below the confluence of these headwaters. The pH here rises sharply—above 7.0 on most occasions—and is matched by up to a tenfold increase in calcium content, as the acid and therefore aggressive water moves onto the Undersett limestone. Although not the highest in the series, this is the first of the Yoredale limestones to be crossed by the stream. The higher Main limestone is present above the Undersett limestone, but only to the south of these headwaters.

It is worth noting that compared to calcium, magnesium shows only a modest increase at site 3 over the headwaters, where its presence is probably derived from the shales.

Between sites 3 and 6, values for all the determinands increase gradually as the water crosses in turn the Middle and Simonstone limestones, and the Lower Lonsdaleia series (the lowest of the Yoredale limestones). At site 6, the stream has in fact been flowing on the Great Scar limestone for 200 m. After another 400 m on this very pure limestone, at site 7, all the determinands, except magnesium, reach their maximum values. The magnesium maxima tend to occur upstream at site 6.

Between sites 7 and 8 the main stream is fed by tributaries from the south side of Darnbrook Fell, which cover a catchment of almost equal size. With few exceptions, mixing with this water causes a marked reduction in all the determinands at site 8.

One hundred metres downstream of site 8 a series of sinks has developed in the stream bed. These are efficient enough to leave the channel dry during baseflows, but under exceptionally wet conditions they are unable to take the high flow allowing the water to continue to its confluence with Cowside Beck. Sampling in March 1981 was carried out during a stormflow event, and although the tributary crossings were impassable, the severe

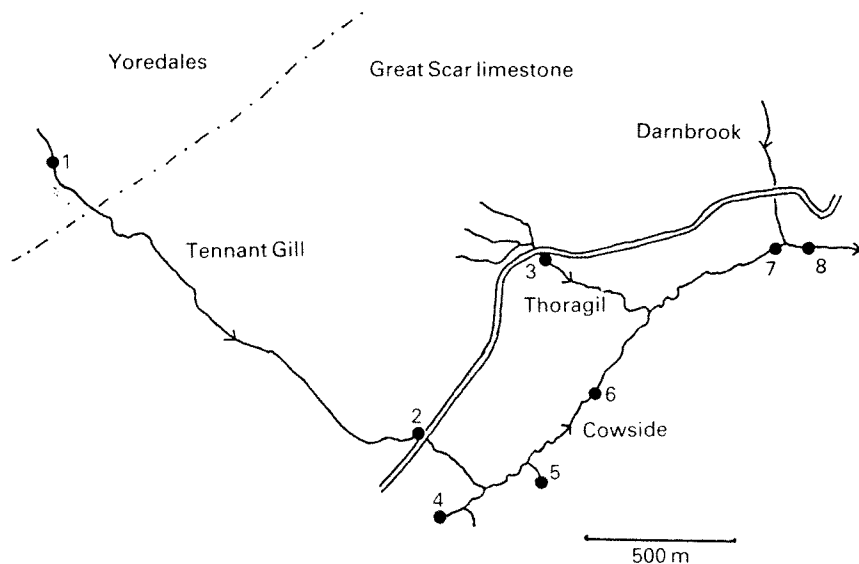


FIG. 9.
Cowside.

dilution and depression of values for all determinands below normal levels is evident at site 8.

Cowside

Cowside Beck runs northeast to the River Skirfare on a valley affected by both glacial and meltwater erosion (Figure 9). Much of the catchment is on Great Scar limestone, with subsurface water flows dominant, particularly on the south side.

The main stream is fed by a series of well-developed springs and risings close to the channel. Those higher up the valley, or the valley sides, are only active after heavy storms cause a rise in the water table. Some, however, maintain surface flow in the stream at all seasons, so it is likely that the Horton slate basement lies just below the present valley floor.

Two longer tributaries feed the main stream from the northwest. Tennant Gill rises on Yoredale shale just below the Millstone Grit. To take it out of the meadows on the valley floor it has been contour channelled along the lower part of its course, where it crosses onto drift covering Great Scar limestone. In 1982, however, a sink developed just above Tennant Gill farm and the lower section has since been mostly dry. A number of smaller streams also run over the Yoredales and drift to sink into the Great Scar limestone below. These are presumed to reappear at risings in the main valley, although the precise linkages have still to be traced.

Thoragill Beck is also in a valley affected by meltwater erosion. It rises from springs within the Great Scar limestone and runs for 750 m to its confluence with Cowside.

Sampling sites 1 and 2 were on Tennant Gill, the first before the stream moves off the Yoredales and the second on the drift cover over the Great Scar limestone. These waters consistently have lower values for conductivity, alkalinity, calcium and total hardness, providing a clear contrast between these sites and the others in the system which are directly on Great Scar limestone. Magnesium values are, however, normally the highest found in this system, perhaps reflecting high magnesium content in the Yoredale shales.

Thoragill Beck was sampled after the confluence of its three headwaters at site 3. These springs rise near the top of the Great Scar succession, and with all the determinands except magnesium higher, provides a useful contrast to Tennant Gill. pH values are consistently the highest within the Cowside system, and with very few exceptions also usually the highest of all the running water sampled.

Sites 4 and 5 are two risings close to the main section of Cowside Beck. Despite being on opposite sides of the valley, their characteristics are very similar. Values for conductivity, alkalinity, calcium and total hardness are usually higher than at Thoragill, probably reflecting a longer flowthrough time within the limestone.

Sites 6, 7 and 8 lie on the main section of Cowside Beck. On most occasions, when Darnbrook Beck was dry at the confluence, all the determinands except pH show very little change downstream from the risings. All, however, show a marked depression at site 8 in July 1981, illustrating that when water does reach here from the Darnbrook catchment, there can be a strong dilution effect.

The increase in pH that is usually observed downstream may be due to a combination of factors: loss of carbon dioxide to the atmosphere soon after water emerges from the risings and photosynthetic uptake of carbon dioxide by aquatic plants. Both will reduce the acidity of the water. Although the pH changes might be expected to be more pronounced in summer when primary production is higher, it is difficult to discern this trend.

Trends in the calcium, alkalinity and total hardness values for sites 3–5 (Thoragill and the two risings) show a late summer maximum and winter minimum, suggesting a seasonal variation in limestone dissolution. Pitty (1966) related this to an increase in bacteriological activity and carbon dioxide production in the plant root zone as soil temperatures rise during summer months. The carbon dioxide reacts with water to form unstable carbonic acid which dissolves calcium carbonate, the principal constituent of limestone, to produce the soluble calcium bicarbonate.

Gordale

Gordale Beck is the major south flowing stream in the study area (Figure 10). It rises as a large spring pool within Great Close Mire, and further springs around Middlehouse make a contribution to the flow as does the stream which joins the beck from the east just above the Mastiles Bridge ford. The relatively high drainage density at Great Close Mire is related to the proximity of the slate basement. The main stream crosses the North Craven fault onto the Great Scar limestone, near the ford at Mastiles bridge. South of here it flows through a gorge cut back from the Mid Craven fault scarp by meltwater erosion. Two waterfalls lie close to each other in the steepest section of the gorge. Although some minor sinks have developed in the stream bed, downstream there is also significant redeposition of calcium carbonate as tufa, which allows some of the water to remain as a surface stream in most seasons.

In almost all instances, the headwater sites 1 and 2 at Great Close Mire, and above the ford, have higher values for all determinands than the risings and main stream in the Cowside system. A similar observation was made by Pentecost (1981) comparing Gordale Beck with Waterfall Beck, a north flowing tributary of Cowside entering just below the confluence with Darnbrook. This pattern may be explained by the fact that Gordale is predominantly a south facing catchment. Higher mean soil temperatures and carbon dioxide production are again reflected by higher weathering potential and rates of limestone dissolution.

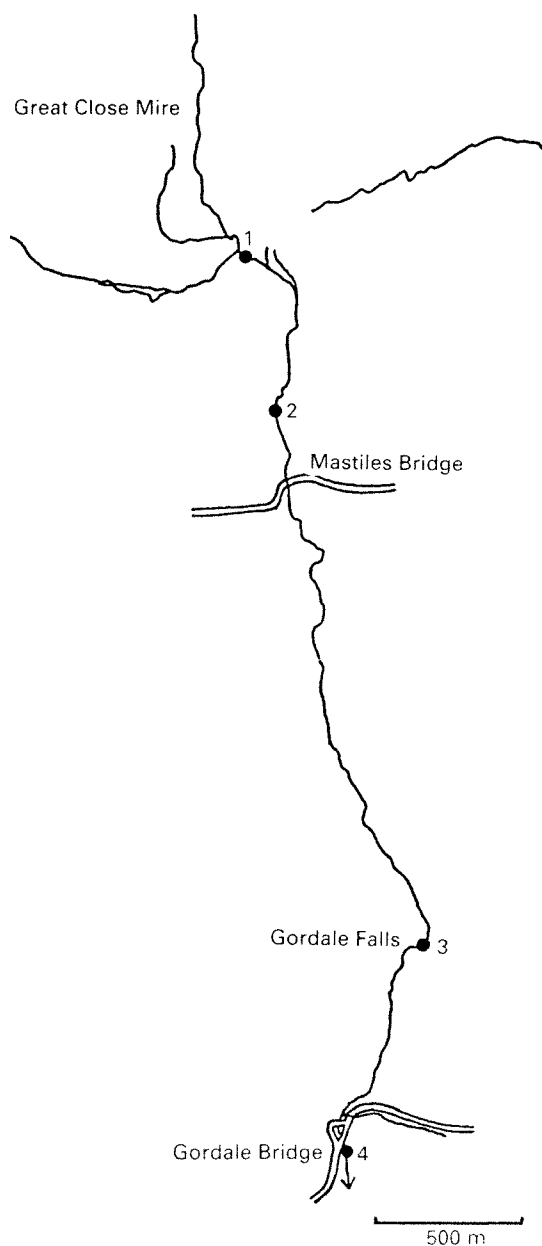


FIG. 10.
Gordale.

A further significant observation within the Gordale system is the loss of carbonates and bicarbonates (shown by decreases in alkalinity); decreases in calcium; and an increase in pH. These all occur between site 2 in Upper Gordale and site 3 below Gordale falls. These differences reflect the diffusional loss of carbon dioxide to the atmosphere, in particular where the beck plunges over the waterfalls, and the photosynthetic activity of the aquatic

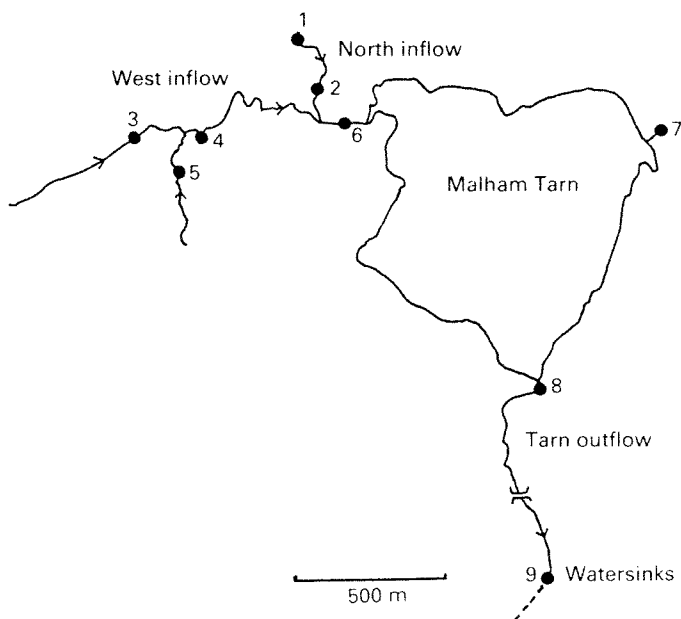
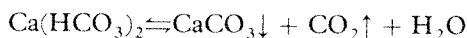


FIG. 11.
Malham Tarn.

plants. In each case the removal of carbon dioxide upsets the chemical equilibrium and precipitation of calcium carbonate in the form of tufa:



Compared to Gordale, tufa deposition is significantly absent in Cowside Beck. Pentecost (1975) remarked on the absence of deposition downstream from the confluence with Darnbrook Beck. There is also no visible evidence of deposition upstream from here either. This is confirmed by the lack of depression in the calcium and alkalinity values along the main section of the stream. This upstream absence of tufa could be attributed to the biochemical activity within the soil. Gordale Beck has its risings on the warmer south-facing slopes of Malham Moor while the catchment area of Cowside includes the cooler northern slopes, and the higher ground of Fountains Fell. This difference in soil temperature will affect the bacteriological activity of the soil resulting in a lower carbon dioxide production in the plant root zone for Cowside. The underground water emerging at the Cowside risings will therefore have smaller concentrations of carbon dioxide and calcium (Appendix 5) and hence have a less tendency to precipitate calcium carbonate from solution than for Gordale.

Malham Tarn

The Tarn, its inflow and its outflow streams all reflect the proximity of the slate basement (Figure 11). The largest inflow feeds the Tarn in the northwest corner, taking water from springs at the base of the limestone slopes to the north and from within the drift mounds to the west. Smaller inflows and seeps also feed the Tarn, with some of the most obvious ones at the base of the slopes above the northeast shore.

The Tarn outflow runs south for about 500 m as a surface stream, crosses the North Craven fault and sinks into the Great Scar limestone in several places. Although Water Sinks is shown on maps at SD 895655, the location of the final disappearance varies with rainfall and with discharge from the Tarn. Low flows sink about 100 m from where the stream crosses under the road, moderate flows continue to Water Sinks and high flows use the valley floor to the south. Two hundred metres along this valley a sink, previously filled in, became prominent again through surface collapse in March 1983.

A good contrast exists between the sites on the north and west inflows. With the exception of pH on a few occasions, sites 1 and 2 on the north inflow have characteristically lower values for all determinands than sites 3–5 grouped on the west inflows. This probably reflects the different routes taken by groundwater to the respective springs and risings—through Great Scar limestone to site 1 and through limestone-rich drift with a longer flowthrough time to sites 3 and 5. The highest pH values for all the inflows consistently occur at site 3 on the far west inflow.

The main inflow, sampled at site 6 after the confluence of the north and west inflows, reflects the mixing of water from these two sources. Except for pH, all its determinands consistently fall between those for the two areas upstream. Mean conductivities for the year at sites 2 and 4 are $317 \mu\text{S cm}^{-1}$ and $422 \mu\text{S cm}^{-1}$ respectively. The mean of these values agrees well with the mean of $353 \mu\text{S cm}^{-1}$ for the main inflow at site 6. This suggests that despite the differences in tributary length, the north and west inflows contribute very nearly equal volumes of water to the main inflow section.

The inflow on the northeast shore at site 7 rises at the base of the Great Scar limestone. Its characteristics are similar to sites 1 and 2 on the north inflow, with comparable mean values for most determinands.

Sites 8 and 9 on the Tarn outflow normally have higher pH values, plus lower conductivity, calcium and total hardness values compared to the inflow sites (the one exception is on the March sampling date when stormflows diluted the inflows strongly). This general pattern is linked to the activity of algae and macrophytes in the Tarn. Removal of carbon dioxide from the water during photosynthesis results in the redeposition of calcium carbonate onto the floor of the Tarn (Pigott & Pigott, 1959), and also onto the plants themselves—those most affected being the *Chara* (stoneworts). These losses from solution are therefore reflected in the outflow water.

Superimposed on this is a more complex seasonal pattern where conductivity, alkalinity, calcium and total hardness in late summer are at their lowest in the Tarn outflow, but at a peak in the main inflow. These trends support observations by Lund (1961) and Pitty (1971).

The low values in the outflow reflect the effects of increased photosynthesis in the Tarn during the summer months and higher water temperatures, both leading to reductions in the carbon dioxide concentration and subsequent calcium carbonate deposition. The higher late summer values for the inflow may again reflect the seasonal variations in limestone dissolution that are linked to changes in soil temperatures. At site 6 on the main inflow alkalinity, calcium and total hardness are all significantly related to antecedent soil temperatures ($p < 0.05$). For site 1 at the north inflow rising the relationships are even stronger ($p < 0.01$).

Relationships between the determinands

It is clear from the analyses of all the running water samples that calcium is the major cation and bicarbonate the major anion. Additional analyses were carried out on selected

Table 2. *Additional analyses on samples collected June 1981. Results in milliequivalents per litre*

System	Darnbrook	Cowside	Gordale	Tarn
Site	7	8	2	6
Ca ⁺⁺	1.57	3.59	3.82	3.77
Mg ⁺⁺	0.08	0.07	0.09	0.17
Na ⁺	0.11	0.15	0.12	0.19
K ⁺	0.01	0.01	0.01	0.01
Total Alkalinity	1.54	3.52	4.00	3.94
Strong acids	0.39	0.35	0.36	0.40

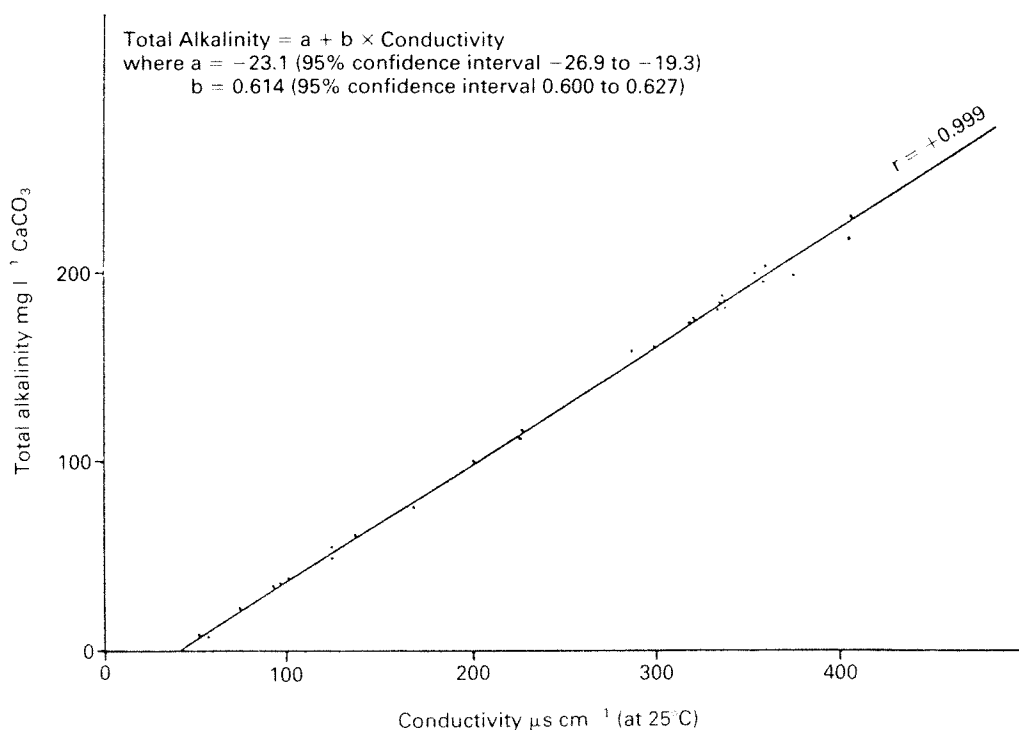


FIG. 12.

The relationship between total alkalinity and conductivity for the running waters sampled 16.6.81.

samples from each system which confirm the dominance of calcium and alkalinity in the total ionic concentration. The results are shown in Table 2.

Another way of expressing this important characteristic of the water chemistry, is to consider the relationships of calcium and alkalinity to conductivity. Figures 12 and 13 graph these using the results from all the running water sites sampled in June 1981. The correlations between these determinands are sufficiently strong ($p < 0.001$) on this and the other occasions that it is possible to derive a fairly reliable estimate of the calcium and alkalinity values for these waters from the graphs, simply by knowing the conductivity values.

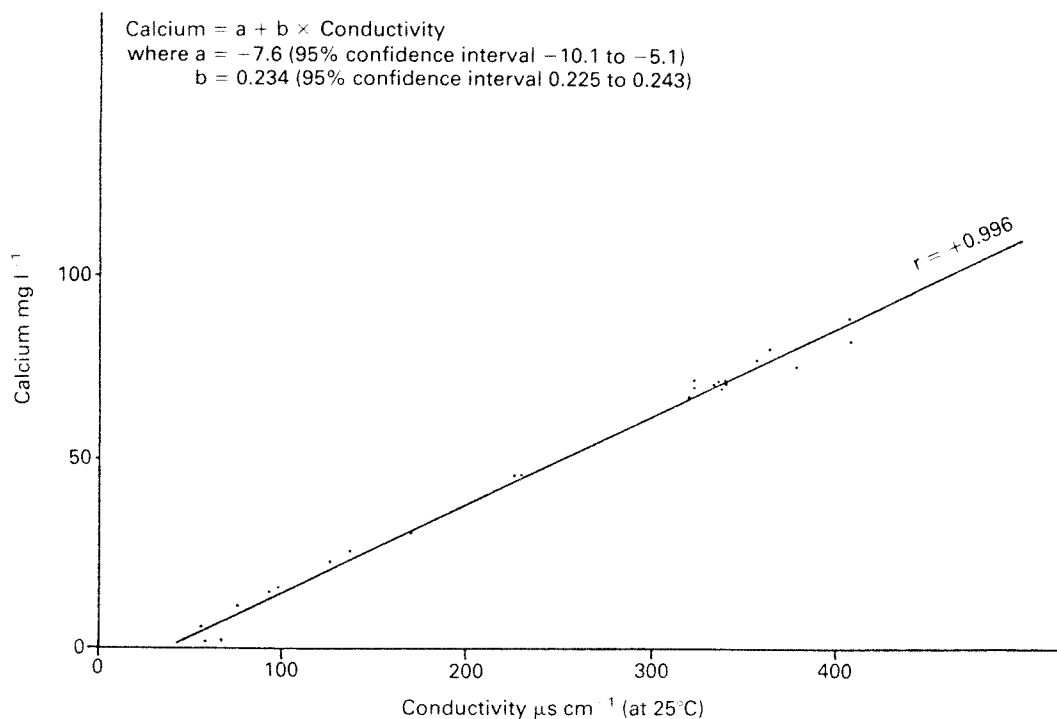


FIG. 13.

The relationship between calcium and conductivity for the running waters sampled 16.6.81.

SUMMARY OF SOME PREVIOUS WORK INVOLVING WATER CHEMISTRY

Water chemistry has been studied in the Malham area since the late nineteenth century. Some of the work concentrated specifically on chemical analysis, but most of the data have been produced to complement other studies.

The Rivers Pollution Commission (1874) analysed samples from the Tarn outflow and risings near Malham village, and reported on their suitability for domestic water supplies. The main determinands were therefore organic impurities, but measurements of total solids, chlorine and total hardness were included. Tate (1879) discussed the source of the River Aire and made the first systematic investigations of the underground flows between the sinks on Malham Moor and risings in Malhamdale. The study revolved mainly around water tracing experiments, but chemical analyses of total solids, organic and volatile matter, inorganic matter, chlorine and degrees of total hardness were given for Water Sinks, Smelt Mill Sinks and Malham Cove Rising in an appendix. Burrell (1900) made a further contribution to this debate on underground flows by producing a "complete mineral analysis" of solids, acids and bases for the same three sites and Airehead Rising. The data from the two previous studies were also given for comparison.

Sledge (1936) gives a measurement of calcium hardness in a study of the aquatic flora of Malham Tarn, but the first systematic long-term sampling programme of the water chemistry of the Tarn was carried out between 1949 and 1953. This complements studies of the algae, Lund (1961), and demonstrates the seasonal cycle of nitrate, phosphate, silicate and alkalinity in the Tarn. Summaries of these results are also given in Round

(1953) and Holmes (1965). The complete analyses from 1951–1953, carried out by F. J. Mackereth at the Windermere laboratory of the Freshwater Biological Association, and data for calcium and magnesium obtained by FBA from the Tarn system in December 1971, are presented as previously unpublished data in Appendices 8 and 9.

To complement studies on bryophytes, Proctor (1960) presents data showing variations in pH, calcium and sodium in surface waters on Tarn Fen and Tarn Moss. In a later study concentrating on the vegetation of the Fen, Proctor (1974) gives data for pH, calcium, magnesium, potassium, sodium and bicarbonate alkalinity for 25 surface water sites, most of them close to those studied in 1960. Adam *et al.* (1975), also analysed surface waters on Tarn Moss and Tarn Fen during phytosociological studies of the vegetation. Data on pH, calcium, magnesium, sodium, potassium and conductivity are presented in an unpublished appendix, available in the Field Centre records, for 45 quadrats taken along transects through the wetland complex.

Detailed karst water studies by Pitty (1968 and 1971) and Ternan (1971) have contributed to the understanding of underground water flows in limestone. Both authors use measurements of calcium hardness to illustrate their findings, with Malham Tarn, Gordale Beck, and springs and risings around Fountains Fell and High Mark (south of Parson's Pulpit) among their sampling sites.

Pentecost (1975) investigated calcium carbonate deposition by blue-green algae and the chemical characteristics of tufa depositing waters throughout the UK. In a further discussion of the tufa deposits of the Malham area, he (1981), summarises some of the chemical data from the previous study. Data on pH, alkalinity, major cations and anions are given for several sources including Gordale Beck, Malham Tarn and tributaries to Cowside Beck. Downstream changes in water chemistry are also related to tufa deposition.

Since 1977 certain aspects of the water chemistry of the Tarn outflow and the main inflow have been monitored by the Yorkshire Water Authority. Data on phosphate-phosphorus; ammonium-, nitrate-, and nitrite-nitrogen; alkalinity, chloride, pH and dissolved oxygen are available in the Field Centre records and sampling continues on a bimonthly basis.

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REFERENCES

- ADAM, P., BIRKS, H. J. B., HUNTLEY, B. and PRENTICE, I. C. (1975). Phytosociological studies at Malham Tarn Moss and Fen, Yorkshire, England. *Vegetatio*, **30**, 2, 117–132.
- AMERICAN PUBLIC HEALTH ASSOCIATION (APHA) (1985). *American Water Works Association and Water Pollution Control Federation, Standard methods for the examination of water and wastewater*. 16th edition, American Public Health Association, Washington DC.
- BURRELL, B. A. (1900). The composition of some Malham waters. *Proceedings of the Yorkshire Geological Society*, **14**, 1, 45–48.
- CLAYTON, K. M. (1981). Explanatory description of the landforms of the Malham area. *Field Studies*, **5**, 389–423.
- DEPARTMENT OF THE ENVIRONMENT (1972). *Analysis of raw, potable and waste waters*. H.M.S.O., London.

- DISNEY, R. H. L. (1975). Review of the management policy for the Malham Tarn Estate. *Field Studies*, **4**, 223–242.
- DOUGLAS, I. (1968). *Field methods of water hardness determination*. British Geomorphological Research Group, Technical Bulletin No. 1.
- GOLTERMAN, H. L., CLYMO, R. S. and OHNSTAD, M. A. M. (1978). *Methods for the chemical analysis of fresh waters*. International Biological Programme (IBP) Handbook No. 8, Blackwell.
- HOLMES, P. F. (1965). The natural history of Malham Tarn. *Field Studies*, **2**, 199–223.
- LUND, J. W. G. (1961). The algae of the Malham Tarn district. *Field Studies*, **1**, 85–119.
- MACKERETH, F. J. H. (1963). *Some methods of Water Analysis for Limnologists*. Freshwater Biological Association.
- MACKERETH, F. J. H., HERON, J. and TALLING, J. F. (1978). *Water analysis: some revised methods for limnologists*. Freshwater Biological Association.
- MORRIS, J., ROBINSON, R. J. and WILSON, D. (1979). Removal of colour, iron, manganese and aluminium from acid moorland waters. *Journal of The Institution of Water Engineers and Scientists*, **33**, 4, 377–389.
- PENTECOST, A. (1975). *Calcium carbonate deposition by blue-green algae*. PhD thesis, University of North Wales, Bangor.
- PENTECOST, A. (1981). The tufa deposits of the Malham district, North Yorkshire. *Field Studies*, **5**, 365–387.
- PIGOTT, M. E. and PIGOTT, C. D. (1959). Stratigraphy and pollen analysis of Malham Tarn and Tarn Moss. *Field Studies*, **1**, 84–102.
- PITTY, A. F. (1968). Calcium carbonate content of karst water in relation to flow-through time. *Nature*, **217**, 939–940.
- PITTY, A. F. (1971). Biological activity and the uptake and redeposition of calcium carbonate in lake waters. *Environmental Letters*, **1**, 103–109.
- PROCTOR, M. C. F. (1960). Mosses and liverworts of the Malham District. *Field Studies*, **1**, 61–65.
- PROCTOR, M. C. F. (1974). The vegetation of the Malham Tarn Fens. *Field Studies*, **4**, 1–38.
- RIVERS POLLUTION COMMISSION (1874). Sixth report. *The Domestic Water Supply of Great Britain*. pp. 42–43, 112–113. H.M.S.O.
- ROUND, F. E. (1953). An investigation of the benthic algal communities in Malham Tarn, Yorkshire. *Journal of Ecology*, **41**, 174–197.
- SHAW, J. (1982). The geology of the area around Malham Tarn, N. Yorkshire. *Field Studies Council Occasional Publication*, No. 3.
- SINKER, C. A. (1960). The vegetation of the Malham Tarn area. *Proceedings of the Leeds Philosophical and Literary Society, Scientific Section*, **8**, 5, 1–37.
- SLEDGE, W. A. (1936). The aquatic vegetation of Malham Tarn. *Naturalist*, 217–219.
- STANDING COMMITTEE OF ANALYSTS (SCA) (1978). *The measurement of electrical conductivity and the laboratory determination of the pH value of natural, treated and waste waters*. H.M.S.O., London.
- STANDING COMMITTEE OF ANALYSTS (SCA) (1979). *Atomic absorption spectrophotometry*. 1979 version; an essay review. H.M.S.O., London.
- STANDING COMMITTEE OF ANALYSTS (SCA) (1981). *Total hardness, calcium hardness, and magnesium hardness in raw and potable waters by EDTA titrimetry*; 1981 tentative methods. H.M.S.O., London.
- STUMM, W. and MORGAN, J. J. (1981). *Aquatic chemistry*, 2nd edition. Wiley, New York.
- TALLING, J. F. and HILTON, J. (1982). *Advisory report on nutrient levels and related ecology of Malham Tarn*. Freshwater Biological Association: unpublished report.
- TATE, T. (1879). On the source of the River Aire. *Proceedings of the Yorkshire Geological and Polytechnic Society*, Vol. 7.
- TERNAN, J. L. (1971). *Karst water studies in the Malham area, north of the Craven fault*. PhD thesis, University of Hull.
- TRUDGILL, S. T. (1985). Field observations of limestone weathering and erosion in the Malham District, North Yorkshire. *Field Studies*, **6**, 201–236.

Appendix 1. Data from standing water sites

Sampling Sites	pH		Cond (25 °C) $\mu\text{S cm}^{-1}$				Tot. Alk. (CaCO_3) mg l^{-1}				Calcium mg l^{-1}				Magnesium mg l^{-1}				Hardness (CaCO_3) mg l^{-1}			
	Aug '80	Apr '81	Aug '81	Apr '81	Aug '80	Aug '81	Aug '80	Apr '81	Aug '81	Aug '80	Apr '81	Aug '81	Aug '80	Apr '81	Aug '81	Aug '80	Apr '81	Aug '81	Aug '80	Apr '81	Aug '81	
Mid Fen	1	4.66	4.96	4.62	29	20	22	0.8	2.0	0.4	3.1	1.1	1.8	0.44	0.23	0.24	9.6	3.6	5.4			
	2	4.40	4.88	4.41	32	21	28	—	1.6	—	2.7	1.1	1.7	0.40	0.25	0.38	8.4	3.6	5.7			
	3	4.24	5.09	4.81	36	24	32	—	2.8	2.4	2.0	1.5	2.5	0.32	0.29	0.41	6.2	4.9	7.8			
	4	5.24	5.32	5.05	27	23	21	2.8	3.6	3.2	3.9	1.9	2.5	0.42	0.34	0.27	11	6.0	7.3			
	5	4.20	6.13	4.64	37	52	25	—	17	0.8	1.9	15	1.8	0.35	0.30	0.30	6.1	39	5.6			
	6	4.13	4.61	4.30	44	29	34	—	0.4	—	2.6	1.1	1.8	0.42	0.27	0.24	8.2	3.9	5.4			
	7	4.37	4.92	4.52	34	22	26	—	1.6	—	2.8	1.0	1.7	0.40	0.21	0.29	8.5	3.4	5.4			
	8	4.37	4.75	4.42	33	22	28	—	0.8	—	2.5	1.0	1.7	0.40	0.21	0.27	7.9	3.4	5.5			
	9	4.18	4.56	4.42	41	26	28	—	—	—	2.2	1.0	1.6	0.39	0.26	0.27	7.1	3.6	5.1			
	10	4.37	4.79	4.85	34	23	64	—	1.2	29	1.9	1.2	27	0.33	0.26	0.85	6.2	4.1	70			
	11	4.16	4.82	4.63	42	23	23	—	1.2	0.8	1.7	1.1	1.6	0.29	0.26	0.25	5.5	3.2	4.9			
	12	4.39	4.52	4.44	29	25	29	—	—	—	2.2	0.87	1.4	0.39	0.20	0.29	7.0	3.0	4.8			
	18	4.28	5.07	4.68	39	24	27	—	2.0	0.8	2.7	1.6	2.1	0.32	0.21	0.24	8.1	5.0	6.3			
	23	4.26	4.81	4.53	38	21	25	—	1.2	—	2.3	0.74	1.3	0.32	0.18	0.20	7.0	2.6	4.1			
	24	6.16	4.60	4.49	41	25	28	11	—	—	8.8	0.74	1.5	0.27	0.18	0.24	23	2.6	4.8			
	25	5.47	4.77	4.40	34	22	37	4.8	1.6	—	6.6	1.0	2.0	0.33	0.17	0.43	18	2.8	6.8			
	26	4.26	4.67	4.50	38	23	32	—	0.8	—	1.9	0.99	2.4	0.35	0.20	0.23	6.1	3.3	6.9			
	27	6.32	7.30	6.66	77	179	125	32	93	64	17	37	30	0.46	0.46	0.83	45	95	78			
	28	6.08	6.44	5.26	48	40	29	13	14	4.0	10	5.3	4.5	0.48	0.19	0.27	27	14	12			
	29	4.91	4.92	4.60	32	23	27	2.0	1.6	0.4	2.9	1.5	2.1	0.34	0.23	0.18	8.7	4.6	6.1			
Spiggot Hill	1	5.26	4.31	4.34	30	30	35	2.8	—	—	3.5	0.4	1.0	0.35	0.15	0.38	10	1.6	4.1			
	2	3.95	4.31	4.55	51	32	30	—	—	0.4	0.45	0.48	1.4	0.35	0.17	0.38	2.6	1.9	5.1			
	3	4.31	4.15	3.98	36	34	57	—	—	—	0.90	0.45	1.2	0.38	0.17	0.47	3.8	1.8	5.0			
	4	6.22	6.72	6.07	74	149	99	44	66	41	19	27	21	0.88	0.68	0.86	50	70	57			
Pinewood	1a	5.62	5.68	5.18	36	29	30	7.2	5.6	4.4	5.8	3.7	11	0.66	0.27	0.77	17	10	31			
	1b	5.91	5.63	5.48	36	29	29	8.0	5.2	6.0	7.0	3.5	11	0.41	0.32	0.95	19	10	31			
	2a	4.92	5.51	5.77	32	24	31	2.0	5.2	6.0	3.6	2.7	10	0.40	0.23	1.0	11	7.8	29			
	2b	5.63	5.27	5.71	32	24	33	6.0	2.8	7.2	4.8	2.3	10	0.41	0.22	1.1	14	6.6	30			
	3a	6.01	6.17	6.27	35	27	46	8.4	6.8	17	5.4	4.1	10	0.43	0.31	1.0	16	12	29			
	3b	6.38	6.22	6.50	47	31	55	16	8.0	24	8.6	4.0	13	0.50	0.28	1.1	24	11	37			
	4a	7.50	6.91	7.14	161	129	130	73	63	66	40	8.6	31	0.92	0.42	1.5	103	23	83			
	4b	7.44	6.26	5.92	87	35	42	31	7.6	10	22	2.4	11	0.73	0.26	1.2	57	7.0	32			
West Fen	1	7.25	7.06	6.64	102	120	125	34	37	52	17	17	22	0.44	0.38	0.63	44	44	58			
	2	7.23	7.09	7.48	313	278	226	134	112	114	55	47	49	0.64	0.58	1.0	139	121	127			
Malham Tarn Fountains Tarn		7.98	8.37	8.59	202	225	195	106	108	103	45	41	48	0.87	0.38	1.3	117	103	126			
		3.92	4.25	4.11	71	47	52	—	—	—	0.90	1.0	0.70	0.40	0.25	0.30	3.9	3.5	2.9			

Appendix 2. *Data from running water systems*

pH

System and Site		26.7.80	28.9.80	30.11.80	1.2.81	8.3.81	19.4.81	16.6.81
Darnbrook	1	4.48	4.22	4.48	4.30	**	**	4.14
	2	4.37	4.31	4.31	4.20	**	4.66	4.29
	3	7.46	6.98	7.28	7.14	**	7.64	6.56
	4	8.25	7.66	7.75	7.68	**	8.24	7.45
	5	8.93	7.90	7.94	7.75	**	8.52	7.78
	6	8.37	8.23	7.91	7.80	**	8.72	7.80
	7	9.13	8.68	8.32	8.37	**	9.07	8.49
	8	9.01	8.22	8.07	8.00	7.30	8.87	8.36
Cowside	1	8.13	7.90	8.10	7.96	7.40	8.18	7.65
	2	8.50	8.03	8.12	8.04	7.66	8.30	8.04
	3	9.07	8.70	8.60	8.73	8.23	8.98	8.69
	4	7.62	7.49	7.66	7.61	7.77	7.61	7.52
	5	7.62	7.53	7.68	7.63	7.88	7.67	7.53
	6	**	**	8.07	8.05	8.03	8.35	7.94
	7	8.55	8.45	8.42	**	**	**	**
	8	8.56	8.43	8.43	8.37	7.50	8.40	8.43
Gordale	1	8.15	8.14	8.22	8.23	8.21	8.40	8.29
	2	8.16	8.17	8.23	8.13	8.13	8.24	8.22
	3	8.34	8.35	8.52	8.35	8.49	8.32	8.42
	4	8.08	8.17	8.22	7.63	8.20	8.20	8.12
Malham Tarn	1	7.48	7.40	7.54	7.56	7.85	7.58	7.37
	2	7.61	7.55	7.74	7.68	7.89	8.01	7.50
	3	**	8.08	8.40	8.25	8.27	**	8.29
	4	7.66	7.50	7.61	7.62	7.71	7.83	7.57
	5	7.69	7.53	7.62	7.58	7.60	7.85	7.65
	6	7.68	7.59	7.77	7.74	7.80	8.08	7.67
	7	7.13	7.45	7.94	7.83	7.81	7.60	7.50
	8	8.77	8.21	8.32	8.27	8.31	8.39	8.54
	9	8.47	8.61	8.40	8.52	8.40	8.25	8.59

Appendix 3. *Conductivity ($\mu\text{S cm}^{-1}$) at 25°C*

System and Site		26.7.80	28.9.80	30.11.80	1.2.81	8.3.81	19.4.81	16.6.81
Darnbrook	1	64	64	57	61	**	**	65
	2	61	58	55	63	**	49	56
	3	120	78	90	86	**	153	54
	4	137	105	104	106	**	162	73
	5	169	122	120	120	**	181	91
	6	380	344	122	125	**	183	96
	7	346	348	231	194	**	240	168
	8	231	163	157	145	50	193	136
Cowside	1	213	178	172	164	60	219	124
	2	214	173	163	161	72	217	124
	3	322	334	306	268	183	268	286
	4	364	371	311	292	202	315	339
	5	359	360	298	281	216	302	335
	6	**	**	313	281	208	303	322
	7	357	355	317	**	**	**	**
Gordale	8	360	358	318	281	68	310	321
	1	399	418	391	365	253	353	362
	2	387	406	373	348	284	353	356
	3	291	364	365	338	249	317	319
Malham Tarn	4	366	375	355	336	252	334	335
	1	367	378	318	288	204	319	336
	2	373	382	316	292	205	320	337
	3	**	441	407	404	312	**	408
	4	515	495	440	423	249	422	407
	5	515	488	446	419	217	415	377
	6	420	417	369	337	213	354	360
	7	367	369	340	330	269	341	339
	8	192	237	261	253	225	240	225
	9	201	239	266	256	225	249	226

Appendix 4. *Total Alkalinity (mg l⁻¹CaCO₃)*

System and Site		26.7.80	28.9.80	30.11.80	1.2.81	8.3.81	19.4.81	16.6.81
Darnbrook	1	—	—	—	—	**	**	—
	2	—	—	—	—	**	0.8	—
	3	36	20	24	22	**	56	8.4
	4	47	37	35	35	**	65	22
	5	66	47	42	44	**	79	33
	6	158	167	46	45	**	80	35
	7	124	177	106	84	**	144	77
	8	91	73	67	59	12	90	62
Cowside	1	89	75	74	69	13	98	50
	2	86	74	70	67	22	98	55
	3	150	175	155	130	88	135	159
	4	166	192	158	140	98	152	185
	5	157	184	145	134	107	141	182
	6	**	**	158	156	102	147	176
	7	161	185	161	**	**	**	**
	8	164	185	159	138	20	149	176
Gordale	1	184	221	204	186	133	177	204
	2	180	213	195	180	154	175	200
	3	126	184	190	174	132	155	173
	4	166	192	181	158	132	163	181
Malham Tarn	1	165	195	157	141	101	154	184
	2	168	194	159	142	101	158	188
	3	**	235	217	200	157	**	230
	4	231	255	228	210	118	203	218
	5	230	247	228	211	108	203	199
	6	188	214	188	163	104	173	197
	7	142	182	170	164	143	163	182
	8	73	111	127	119	113	113	114
	9	95	114	130	121	113	117	116

Appendix 5. *Calcium (mg l⁻¹)*

System and Site		26.7.80	28.9.80	30.11.80	1.2.81	8.3.81	19.4.81	16.6.81
Darnbrook	1	2.1	1.7	2.1	1.8	**	**	1.5
	2	1.6	1.6	1.3	1.3	**	2.0	1.4
	3	16	12	12	13	**	24	4.8
	4	21	17	15	17	**	25	11
	5	28	19	17	20	**	29	15
	6	72	68	18	20	**	30	16
	7	64	72	43	39	**	44	31
	8	41	31	27	28	7.1	33	26
Cowside	1	39	32	31	30	57	36	23
	2	36	34	29	29	11	36	23
	3	64	76	66	60	36	52	65
	4	70	84	65	63	40	60	72
	5	68	68	60	60	43	59	70
	6	**	**	64	61	42	59	70
	7	70	76	66	**	**	**	**
	8	67	77	65	61	12	59	72
Gordale	1	81	76	80	84	53	68	80
	2	78	64	79	84	59	68	77
	3	56	65	77	79	52	59	68
	4	77	59	72	77	53	61	71
Malham Tarn	1	69	79	60	63	39	60	71
	2	72	77	60	63	41	60	70
	3	**	85	87	90	65	**	88
	4	94	95	92	93	49	79	82
	5	97	92	94	92	42	75	75
	6	81	82	80	72	42	69	76
	7	75	82	68	45	59	66	71
	8	35	33	51	53	46	45	46
	9	36	48	51	56	45	46	46

Appendix 6. *Magnesium* (mg l^{-1})

System and Site		26.7.80	28.9.80	30.11.80	1.2.81	8.3.81	19.4.81	16.6.81
Darnbrook	1	0.75	0.79	0.80	0.96	**	**	0.66
	2	0.96	0.89	1.00	0.80	**	0.79	0.73
	3	1.25	1.12	1.05	1.13	**	1.36	0.73
	4	1.45	1.18	1.21	1.13	**	1.48	0.86
	5	1.92	1.38	1.36	1.27	**	1.92	1.05
	6	1.48	1.75	1.31	1.27	**	1.92	1.05
	7	1.12	1.55	1.11	1.27	**	1.38	1.02
	8	1.19	1.33	0.96	0.93	0.47	1.23	0.90
Cowside	1	1.43	1.69	1.47	1.39	0.45	1.79	1.18
	2	1.63	1.83	1.27	1.32	0.61	1.51	0.97
	3	0.77	1.48	0.78	0.70	0.60	0.82	0.87
	4	0.63	1.24	0.62	0.67	0.54	0.80	0.73
	5	0.63	1.24	0.61	0.67	0.46	0.72	0.68
	6	**	**	0.69	0.76	0.52	0.72	0.80
	7	0.70	1.46	0.62	**	**	**	**
	8	0.61	1.48	0.61	0.78	0.49	0.70	0.90
Gordale	1	1.99	1.73	1.26	1.56	0.73	1.79	1.28
	2	1.19	1.24	0.96	1.21	1.44	1.30	1.06
	3	1.34	1.29	1.21	1.21	0.75	1.30	1.11
	4	1.92	1.75	1.73	1.74	1.04	1.96	1.52
Malham Tarn	1	0.65	1.33	0.62	0.70	0.49	1.09	1.67
	2	0.66	1.17	0.74	0.56	0.49	1.11	1.62
	3	**	1.80	1.38	0.99	1.01	**	2.18
	4	2.11	2.12	1.82	1.13	0.88	2.18	2.65
	5	2.11	2.45	2.11	1.24	1.31	1.92	2.37
	6	1.24	1.46	1.18	0.70	0.64	1.57	2.02
	7	0.68	0.95	0.59	0.36	0.50	0.84	1.52
	8	0.81	1.10	0.92	0.84	0.71	0.84	0.80
	9	0.79	1.10	0.90	0.70	0.79	1.30	0.80

Appendix 7. *Total Hardness* ($\text{mg l}^{-1} \text{CaCO}_3$)

System and Site		26.7.80	28.9.80	30.11.80	1.2.81	8.3.81	19.4.81	16.6.81
Darnbrook	1	8.3	7.5	8.5	8.4	**	**	6.5
	2	7.9	7.6	7.3	6.5	**	8.2	6.5
	3	45	35	34	37	**	66	15
	4	58	47	42	47	**	69	31
	5	78	53	48	55	**	80	42
	6	186	177	50	55	**	83	44
	7	164	186	112	103	**	116	82
	8	107	83	71	74	19	87	69
Cowside	1	103	87	84	81	17	97	62
	2	97	92	78	79	30	96	61
	3	163	196	168	153	92	133	166
	4	177	215	165	160	102	153	183
	5	172	175	152	153	109	150	180
	6	**	**	163	155	106	150	178
	7	178	196	167	**	**	**	**
Gordale	8	170	198	165	156	32	150	183
	1	211	197	205	216	135	177	205
	2	200	165	201	215	153	175	197
	3	145	168	197	202	133	153	174
Malham Tarn	4	200	155	187	200	137	160	184
	1	177	203	152	160	99	154	184
	2	183	197	153	160	104	154	181
	3	**	220	223	229	167	**	229
	4	243	246	237	237	126	206	216
	5	251	240	243	235	110	195	197
	6	207	211	205	183	107	179	198
	7	190	209	172	114	149	168	184
	8	91	87	131	135	118	116	118
	9	93	124	131	143	116	119	118

Appendix 8
Chemical Analyses—Malham Tarn and Main Inflow—1951–1953
All results in mg l⁻¹

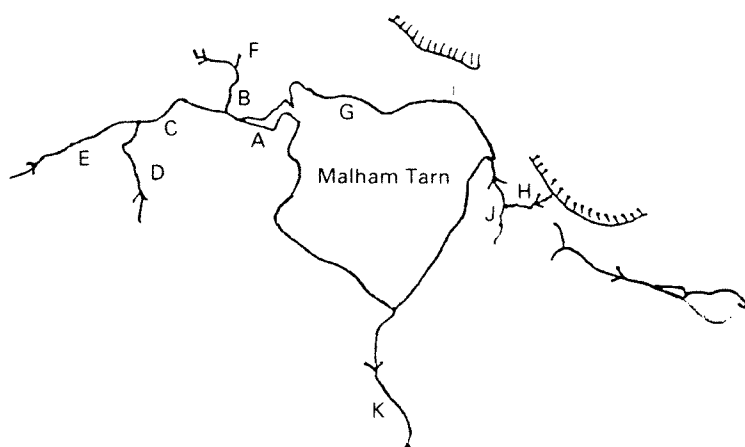
INFLOW					TARN			
Date	SiO ₂	NO ₃ N	PO ₄ P	Alkalinity as CaCO ₃	SiO ₂	NO ₃ N	PO ₄ P	Alkalinity as CaCO ₃
1951								
24 Apr	0.90	0.09	0.001	166	0.50	0.13	0.001	116
8 May	1.10	0.02	<0.001	139	0.25	0.07	<0.001	116
19 May	0.80	0.40	<0.001	172	0.30	0.05	<0.001	116
8 Jun	0.50	0.14	0.001	171	0.30	0.02	<0.001	124
26 Jun	0.57	0.25	<0.001	182	0.35	0.01	<0.001	111
9 Jul	1.00	0.22	<0.001	132	0.43	0.02	<0.001	102
23 Jul	1.30	0.36	<0.001	191	0.90	0.03	<0.001	92
6 Aug	1.00	0.18	<0.001	185	0.72	0.03	<0.001	85
17 Aug	1.70	0.04	0.001	168	0.90	0.03	<0.001	80
13 Sep	1.70	0.03	<0.001	218	0.90	0.02	<0.001	88
27 Sep	1.70	0.02	<0.001	216	1.10	0.02	<0.001	93
10 Oct	1.70	0.38	<0.001	218	0.88	0.03	<0.001	98
29 Oct	1.40	0.27	<0.001	209	0.75	0.02	<0.001	97
5 Nov	1.50	0.08	<0.001	165	0.75	0.03	<0.001	97
12 Nov	1.50	0.50	<0.001	140	0.90	0.02	<0.001	105
26 Nov	1.60	0.27	<0.001	166	1.00	0.17	<0.001	116
17 Dec	1.50	0.10	<0.001	152	1.40	0.23	<0.001	127
1952								
25 Feb	1.30	0.29	<0.001	136	1.00	0.27	<0.001	111
10 Mar	1.30	0.22	<0.001	160	0.70	0.24	<0.001	110
4 Apr	1.60	0.45	<0.001	175	0.60	0.20	<0.001	112
21 Apr	1.10	0.30	<0.001	164	0.18	0.18	<0.001	117
19 May	1.10	0.07	0.001	176	0.25	0.07	0.001	116
9 Jun	0.90	0.03	0.001	185	0.22	0.02	<0.001	98
7 Jul	1.00	0.09	<0.001	178	0.50	0.02	<0.001	93
25 Jul	1.80	0.13	0.003	198	1.10	0.02	0.002	87
12 Aug	1.90	0.05	—	221	1.40	0.02	—	100
8 Sep	1.50	0.17	0.001	175	0.90	0.03	0.001	98
6 Oct	1.80	0.24	0.001	203	0.90	0.03	0.001	108
13 Nov	1.70	0.24	0.001	188	0.90	0.08	0.001	115
16 Dec	1.80	0.30	0.0015	163	0.90	0.09	0.0015	129
1953								
19 Jan	1.80	0.37	0.003	151	1.00	0.14	0.002	128
4 Mar	1.80	0.33	0.002	177	0.75	0.15	0.0015	121
9 Apr	1.80	0.24	0.001	136	0.63	0.03	0.001	120
23 Apr	1.00	0.25	<0.001	156	0.21	0.02	<0.001	123
6 May	0.75	0.20	<0.001	159	0.26	<0.02	<0.001	121
9 Jun	0.86	0.20	0.0015	155	0.31	0.04	0.002	102
7 Jul	1.80	0.17	0.001	210	0.90	0.03	0.001	99
29 Jul	1.80	0.15	0.002	198	1.10	0.02	0.0025	103
17 Aug	1.28	0.14	0.002	207	0.59	0.02	0.001	101
7 Sep	2.20	0.10	0.001	231	1.00	0.03	0.001	121
28 Sep	2.10	0.03	<0.001	220	1.60	0.03	<0.001	122
19 Oct	2.00	0.13	<0.001	203	1.00	0.03	<0.001	130
16 Nov	2.20	0.25	0.001	201	1.70	0.03	0.001	136
14 Dec	2.40	0.19	0.003	158	1.90	0.03	0.002	142

Methods

SiO ₂	Colorimetric determination by comparison with standards of Picric acid (Mackereth, 1963).
NO ₃ N	Colorimetric determination using phenoldisulphonic acid (Mackereth, 1963).
PO ₄ P	Colorimetric determination by comparison with standards using Deniges reagent and stannous chloride solution (Mackereth, 1963).
Alkalinity	Titrimetric determination using standard acid and BDH 4,5 Indicator (Mackereth <i>et al.</i> , 1978).

Appendix 9

Analysis of Water Chemistry—Malham Tarn Area—December 1971

All results in mg l^{-1} 

Site	Ca^{++}	Mg^{++}	$\text{Ca}^{++}/\text{Mg}^{++}$
A	81.0	1.26	64
B	77.0	0.92	84
C	105.0	2.25	47
D	108.0	2.23	48
E	90.0	2.30	39
F	76.0	0.93	82
G	60.0	1.00	60
H	82.0	0.66	124
J	92.0	0.84	110
K	57.0	1.02	56

Methods

All analyses by Atomic Absorption Spectrophotometry.