

**Sunbiggin Tarn & Moors & Little Asby Common SSSI water quality
monitoring survey**

Stephen C. Maberly, Mitzi M. DeVille, J. Ben James, Patrick O. Keenan &
Stephen J. Thackeray

Lake Ecosystems Group
UK Centre for Ecology & Hydrology
Lancaster Environment Centre
Library Avenue
Bailrigg
Lancaster LA1 4AP

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EXECUTIVE SUMMARY

1. Sunbiggin Tarn is a small marl lake on the Orton fells in North West England, where there is concern about nutrient levels and consequent algal growth that places the lake in an ecologically unfavourable state. This work was designed to investigate the causes of this nutrient enrichment based on monthly samples from seven inflow streams and the lake between April 2019 and February 2020 and a depth profile measured in mid-summer.
2. There are several lines of evidence for calcite precipitation in the tarn during summer. Alkalinity in summer is lower than in the winter; the tarn alkalinity in the winter is similar to the inflowing streams but lower than the streams in the summer; calculations show that the calcite was highly oversaturated in summer; finally, data from the Environment Agency from 2004 to 2006 show summer concentrations of dissolved calcium are about half that of winter concentrations.
3. There is some evidence for internal loading of total phosphorus during the summer since surface concentrations in May, June and July are higher than at other times of years. More frequent depth profiles would be needed to determine if this resulted from internal loading. The current data and calculations suggest that anoxia-triggered release of phosphorus from the sediment is likely to be more important than release of phosphorus from apatite dissolution at depth in producing the high concentrations of soluble reactive phosphorus measured at the bottom of the tarn.
4. The concentration of total phosphorus in the tarn seems to be consistent with the stream concentrations, although the effects of any groundwater inputs are unknown. In contrast, there is a large loss of total nitrogen within the tarn since the concentrations are much lower in the tarn than the inflowing streams.
5. The concentrations of total phosphorus in 2019-2020 was lower than in 2003 and 2004-2006 and the mean and median concentrations of phytoplankton chlorophyll *a* were lower in 2019-2020 than in 2004-2006 but slightly higher than in 2003. There is therefore some suggestion that the ecological conditions in the tarn are improving.
6. The concentrations of nitrate in the tarn are unlikely to inhibit charophyte growth directly but could have an indirect effect by stimulating phytoplankton and epiphytic algae growth that could shade the charophyte beds. The generally low concentrations of nitrogen in the tarn suggest that this is unlikely. Rather primary production could be limited by nitrogen rather than phosphorus, at least in some seasons.
7. More detailed, targeted future investigations are suggested to address some of the uncertainties noted in order to produce more evidence-based knowledge for the conservation and management of Sunbiggin Tarn.

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INTRODUCTION

Sunbiggin Tarn is a small marl lake on the Orton fells in North West England. It is included in the Sunbiggin Tarn and Moors and Little Asby Scar Site of Special Scientific Interest (SSSI) and designated as a Special Area of Conservation (SAC), as an example of habitat 3140 'hard oligo-mesotrophic waters with benthic vegetation of *Chara* and freshwater plants. (Natural England 2013). Although it is a SSSI, several reports record concern over the nutrient levels in the lake. In particular, concentrations of total phosphorus exceed those typical of an unimpacted marl lake and appear to have caused algal growth and changes in macrophyte abundance and composition that places the lake in an ecologically unfavourable state (Bennion et al. 2009; Goldsmith et al. 2003; Pentecost 2013).

The surface water catchment lies in a karst landscape dominated by a bedrock of Lower Carboniferous Yoredales series limestone with sandstones and superficial glacial alluvium and till (Holdgate 2016; McCormack 2003; Natural England 2013). Because this is a karst environment, the surface catchment will not necessarily represent the complete watershed and groundwater inputs, occur- and one of the features of the tarn, tufa formations produced by springs, indicate a groundwater input (Holdgate 1955; Natural England 2013). Potentially, the groundwater could derive from outwith the surface drainage catchment, but the extent of the groundwater catchment is unknown.

The surface water catchment was defined using the UKCEH Flood Estimation Handbook Software and is shown in Fig. 1A. It has an area of 1.83 km², an average elevation of 305 m and is largely south-facing (Table 1). Compared to the nearby English Lake District to the west, the average annual rainfall is relatively low: it was 1.3 m per year in the 1961-1990 reference period (Table 1) compared to 2.2 m in the Windermere catchment. The landcover in the Subiggin catchment is primarily heather-grassland (55.7%) with smaller areas of acid grassland (32.8%), improved grassland in the north-west of the catchment (4.1%) and rock (7.2 %) (Fig. 1B) (UKCEH Land Cover Map 2007, derived from UKCEH UK Lakes Portal, <https://eip.ceh.ac.uk/apps/lakes/>).

The tarn itself, at the bottom of the catchment, lies at an elevation of 255 m (Table 1). It has an area of 4 ha, and a maximum depth of 10 m. An earlier bathymetric survey in 1950 (Holdgate 2016) reported a maximum depth of 11 m, the difference could be caused by water level changes, location of survey readings or a subsequent external inputs or reworking of the marl sediment already within the tarn. Using the contemporary estimated sediment accumulation rate of 4.5 cm y⁻¹ (Goldsmith et al, 2003) the tarn could only have reduced in depth by about 0.3 m over the last 70 years. Assuming that surface water exchange is the only cause of water gains

and losses to the tarn and assuming a standard 25% loss of rainfall input by evapo-transpiration, the annual average retention time is about 300 days, which is quite long for a lake of this size. Obviously, this does not consider the unknown effects of groundwater exchange.

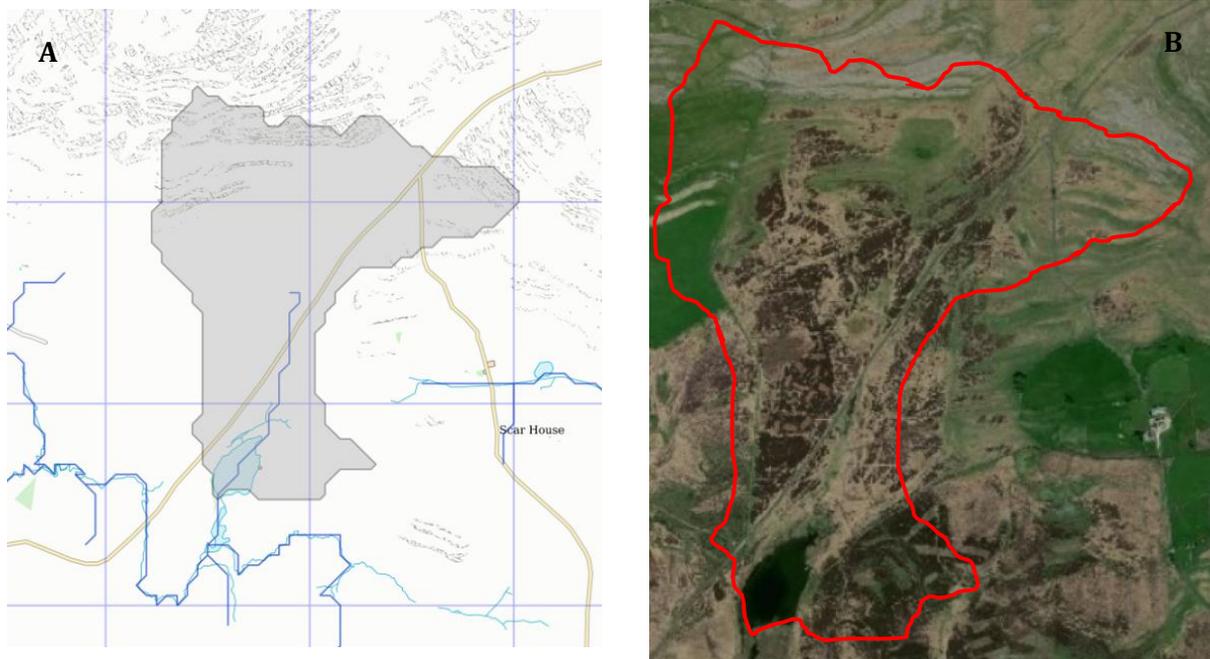


Figure 1. The surface-water catchment of Sunbiggin Tarn. **A**, catchment taken from the UKCEH Flood Estimation Handbook Web Service. Contains OS data © Crown copyright and database right (2020). **B**, Satellite image of the catchments with catchment outline drawn manually.

The Environment Agency undertook roughly monthly sampling on the tarn between July 2004 and December 2006. Two extremely high concentrations of TP were removed from the dataset and median values were calculated to minimise further effects of any spurious extreme values. The data confirm the very high alkalinity in the tarn, with very low concentrations of total N and total oxidised nitrogen (TON, the sum of nitrate and nitrite). The median value of TON of 0.20 mg L^{-1} appeared to be the limit of detection in these analyses, suggesting that TON concentrations could be even lower and that nitrogen could be the limiting nutrient in this lake. The median concentration of TP at 0.029 mg L^{-1} and phytoplankton chlorophyll *a* at $8.1 \text{ } \mu\text{g L}^{-1}$ are higher than might be expected for a marl lake. For example, data from another marl lake, Malham Tarn (albeit with different targets because it is shallower and also with some ecological concern), from the same data source, but over a longer time period, recorded median concentrations of TP and phytoplankton chlorophyll *a* of 0.012 mg L^{-1} and $3.8 \text{ } \mu\text{g L}^{-1}$ respectively. Figures plotted in Talling & Parker (2002) for Malham Tarn from 1985 to 1987

indicate median concentrations of TP and chlorophyll a of 0.015 and mg L⁻¹ and 3.8 µg L⁻¹ respectively.

Table 1. Characteristics of the Sunbiggin Tarn catchment and tarn derived from the UKCEH Lakes Portal and UKCEH Flood Estimation Handbook.

Characteristic	Value
Catchment area (km ²)	1.83
Average catchment elevation (m)	305
Mean catchment slope (Degrees)	5.55
Mean direction of catchment slope (Degrees)	181
Base flow index (revised 2019; index)	0.512
Mean annual rainfall (1961-1990) (m)	1.30
Tarn elevation (m)	255
Tarn area (ha)	4
Tarn perimeter (km)	1
Mean depth (m)	4
Maximum depth (m)	10
Tarn volume (m ³)	144,460
Nominal mean retention time (day)*	296

Assumes only surface-water exchange and evapo-transpiration losses of 25%.

Table 2. Median value and number of water samples from Sunbiggin Tarn between July 2004 and December 2006. Data from the Environment Agency.

Variable	Median	Number of samples
Alkalinity (mequiv L ⁻¹)	2.89	24
Total P (mg P L ⁻¹)	0.029	25
Orthophosphate (mg P L ⁻¹)	0.004	27
Total N (mg N L ⁻¹)	0.491	29
Total oxidised N (mg N L ⁻¹)	0.20	29
Reactive silica (mg SiO ₂ L ⁻¹)	1.13	29
Phytoplankton chlorophyll <i>a</i> (µg L ⁻¹)	8.1	23

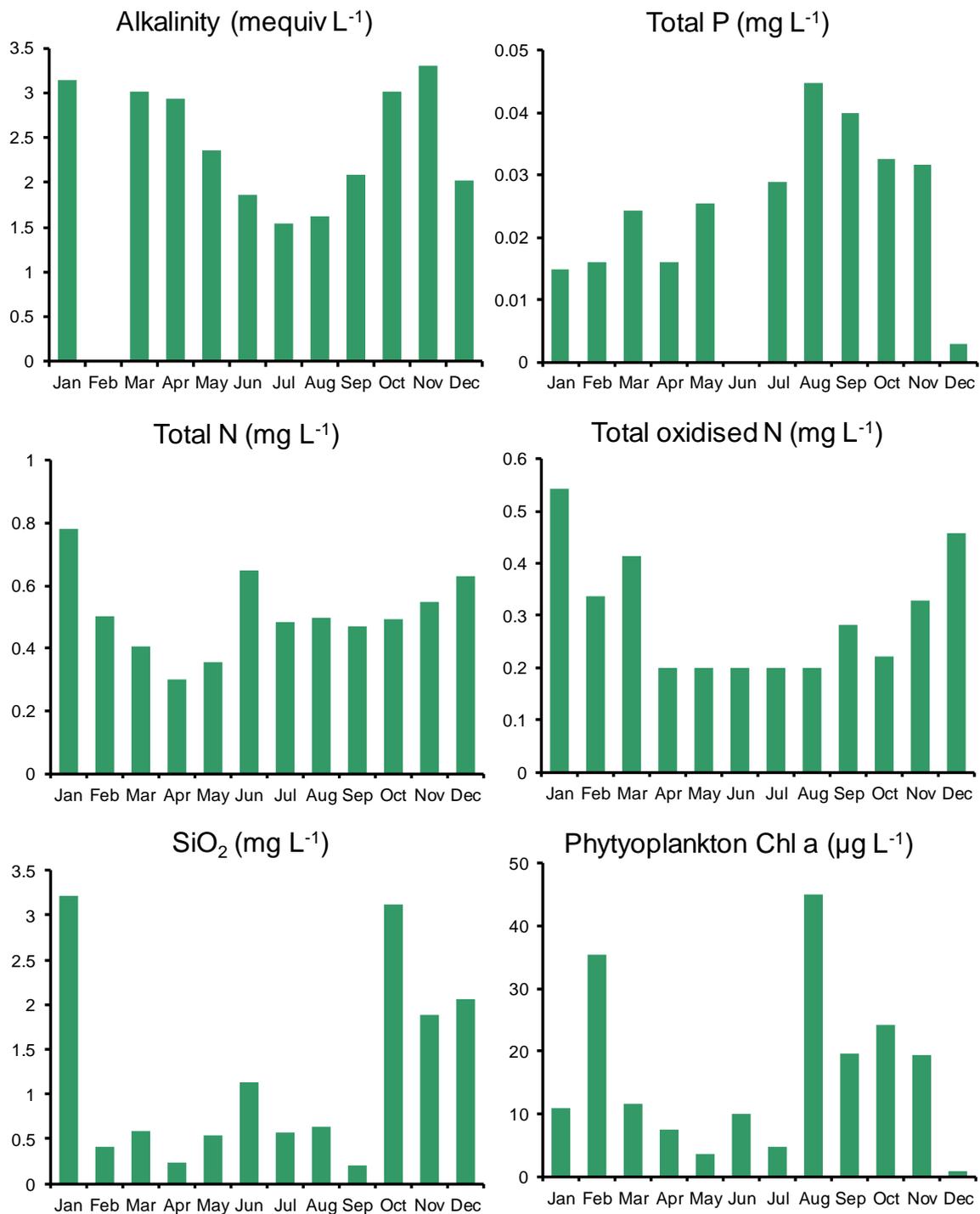


Figure 2. Seasonal patterns of key water quality variables for Sunbiggin Tarn. Data were collected by the Environment Agency between July 2004 and December 2006. Two very high concentrations of total P were excluded from the analysis.

Seasonal patterns of key water quality variables from the Environment Agency data for Sunbiggin Tarn are plotted in Fig. 2. Alkalinity shows a seasonal pattern of reduced alkalinity in

summer which is consistent with calcite precipitation that can be generated by slightly elevated pH that increases the concentration of carbonate that can react with calcium and precipitate. Phosphate can co-precipitate with calcite, as apatite, leading to removal of phosphorus from the water column (Otsuki & Wetzel 1972). Equally, if the apatite dissolves, phosphate will be released back into the water column. The concentration of total P increased during the year, reaching a peak in August that could be consistent with this process, but other mechanisms such as P-release from the sediment or input from the catchment are also possible.

Purpose of the work

The invitation to tender specified that the purpose of this project was to investigate the nutrient status of Sunbiggin Tarn because of concerns that it has become nutrient enriched, potentially damaging the macrophytes that are an intrinsic part of and one of the notified features of the SSSI. The specific topics required in the invitation to tender are listed below:

1. Whether marl formation is likely to be occurring within the lake.
2. Whether there is a summer increase in TP indicative of internal loading
3. Whether lake and spring nutrient concentrations follow similar patterns throughout the year, so is the lake responding to external as opposed to internal loads. Does the lake TP concentration increase in winter in line with concentrations in the springs or does it increase in contrast to the springs suggesting dissolution in lake or other catchment sources. Trends in lake pH will give an indication of the likelihood of dissolution.
4. Whether the lake nutrient concentration is moving in the right direction, has it declined since previous reports and is it approaching the target.
5. Whether there are visible signs of filamentous algal growth and how they fit with the water quality data collected.
6. Whether nitrogen concentrations are at levels that may inhibit charophyte growth (above 2 mg L⁻¹), or whether they are at levels that limit other algal growth.
7. If there is sufficient money for chlorophyll analysis this should be investigated in relation to nutrient conditions.
8. Additional interpretation of the data to understand the cause for the condition of the lake beyond these bullet points is also welcome.

METHODS

Sampling sites

The location of the sampling sites were determined during a site visit with Jan Darrall (Friends of the Lake District), Ruth Hall (Natural England), Deborah Land (Natural England) and Sir Martin Holdgate and are a subset of sites surveyed earlier (Pentecost 2013). The locations are NY67752 07681 for the lake shore, NY67717 07601 for site A, NY67755 07699 for site B, NY67881 07838 for site C, NY67798 07972 for site D, NY67736 07931 for site E, NY67595 07804 for site F and NY67531 07717 for site G (Fig. 3). Sites A to G are equivalent to sites 19, 13, 12, 10, 6, 5 and 3 respectively in Pentecost (2013). In addition, depth profiles were made at the deepest part of the lake (Fig. 3) on 23 July 2019.



Figure 3. Sampling sites at Sunbiggin Tarn. The satellite image shows the location of the seven stream inflows (A to G), the littoral lake sampling site (L) and the mid-lake sampling site (dropped pin).

Monthly measurements on the streams and lake

Monthly measurements were made at the lake littoral and at seven inflows, starting in April 2019 (Fig. 3). The final measurement, completing the 12-month survey planned for March 2020, was prevented by fieldwork restrictions caused by the coronavirus outbreak. On arrival at the tarn, cloud cover (octa) and wind direction and strength (Beaufort scale) were noted and the combination pH-electrode and field meter (Radiometer PHM201) was calibrated with buffers at pH 7 and 10. River discharge data from Lune Bridge on the Lune, the nearest downstream site

from the National River Flow Archive records, were analysed and the average discharge for the five days before each sampling occasion was calculated as an estimate of flow conditions.

At each site, a water sample was collected and where necessary, because low water level made collection difficult at some sites, passed through a coarse mesh to remove large particles. At the streams the sample was taken by dipping a bottle into the water, at the tarn we waded into the water and collected sub-surface water with a bottle on the end of a long pole (~3 m). A water sample in a glass bottle with a ground-glass stopper to prevent air-exchange was collected from the tarn to measure alkalinity. Water samples were stored in a cool box during transit to the laboratory. Additional water samples were collected at each site and temperature, pH and specific conductivity (Hanna 99300) recorded immediately. At each site, photos were taken as a record of the condition and amount of algal growth. Although not specified in the contract, on one occasion (31/20/2019) flow velocity was adequate at four inflows (B, C, D and E) to estimate discharge. The depth and width of the channel was measured and flow rate was measured in triplicate at 2/3rd of the channel depth with an OTT flow meter (Z30). Discharge was calculated as the product of width, flow and velocity using the manufacturer's calibration provided to convert propeller revolutions per minute to flow velocity.

Sampling on the tarn

On 23/07/19, a boat was used to collect depth profiles on the tarn (Fig. 3). A portable echo sounder was used to locate the deepest point on the tarn. A Secchi depth reading was taken (white 30 cm disc) and a depth profile of oxygen and temperature recorded (YSI ProODO). Discrete water samples were collected above and below the thermocline (0, 2, 5, 8 and 8.5 m) using a Freidinger closing bottle sampler and the samples returned to the laboratory where conductivity, and soluble reactive phosphorus concentration were measured. An integrated water sample over the top 5 m was also collected and used to measure phytoplankton chlorophyll concentration and species composition (sample preserved on site with Lugol's iodine) and cell density.

Laboratory measurements and calculations

Alkalinity was measured by Gran titration with ~0.1 M HCl (Mackereth et al. 1978). Soluble reactive phosphorus was determined following Mackereth et al. (1978). Total Phosphorus (TP) was analysed using a K₂S₂O₈ digestion and subsequent molybdenum blue colorimetric analysis, was carried out on a SEAL AQ2 discrete analyser. Unfiltered water samples were digested with K₂S₂O₈ and 1N sulphuric acid and placed in an autoclave under heat and pressure to complete

the digestion procedure. Phosphorus was determined using molybdenum blue chemistry with the addition of ascorbic acid to control the colour production. Calibration and reference standards were prepared and digested in the same manner as the samples. Total Nitrogen (TN) was measured on unfiltered water samples using a Shimadzu TOC-L analyser, equipped with a TNM-L module. TN was combusted at 720°C, with a catalyst, to convert all nitrogen species to nitric oxide. The nitric oxide was measured by a chemiluminescent reaction with ozone. There were two calibration ranges for the instrument, which combined cover a range of 0-10 mg L⁻¹ for nitrogen. Samples with values greater than the highest calibrant were diluted within range using 18.2 MΩ deionised water. Reference samples at three relevant concentrations across this range were used to check the calibration.

Phytoplankton chlorophyll *a* was measured spectrophotometrically after filtering through Whatman GF/C filter paper and extraction in boiling methanol (Talling 1974). The phytoplankton samples preserved in Lugol's iodine were transferred to a counting chamber and the algae were enumerated as described by Lund et al. (1958). Microplankton and nanoplankton were counted at x100 magnification and x400 magnification respectively. The counts were converted to numbers mL⁻¹. Concentrations of inorganic carbon species and calcite solubility were calculated from temperature, pH, alkalinity and ionic strength using the equations in Maberly (1996).

RESULTS & DISCUSSION

The general conditions prevailing at the time of sampling are shown in Table 3.

Table 3. Meteorological and flow conditions on the sampling occasions. Discharge is the mean of the previous five days.

Date	Time	Cloud cover (octa)	Weather	Wind speed (Beaufort scale)	Discharge at Lunes Bridge ($\text{m}^3 \text{s}^{-1}$)*
23/04/2019	15:30	1	Moderate ENE breeze, dry	4	2.06
20/05/2019	10:30	4	Light N breeze, dry	1	1.12
17/06/2019	11:07	5	Fresh SE breeze, dry	5	1.25
23/07/2019	10:05	7	Gentle SSW breeze	3	0.32
29/08/2019	10:30	7	Moderate SSW breeze, dry	4	5.00
03/10/2019	10:20	8	Light SSW breeze, dry	1	2.01
31/10/2019	10:05	1	Fresh ESE breeze, dry	5	1.64
28/11/2019	10:00	8	Gentle NE breeze, rain	3	2.78
18/12/2019	10:15	7	Light SE breeze, dry	1	10.56
23/01/2020	10:35	8	Light SW breeze, dry	1	2.47
27/02/2020	10:32	1	Light SW breeze, dry	2	4.23

Temperature

The surface temperature at Sunbiggin Tarn followed the expected seasonal cycle. The irregular pattern of temperatures in Sunbiggin Tarn is probable caused by measurements near the shore rather than at the open water. The surface temperature of the tarn was generally cooler than at nearby lakes in the English Lake district (Fig. 4). In July, when temperature was measured at the centre of Sunbiggin Tarn, it was about 2.1°C lower than in the English Lake District. This is broadly expected, although slightly larger than that derived from the elevation difference (Layden et al 2015, about 0.8°C for an elevation difference of 215 m). A comparison of the tarn surface temperature with that of the inflowing streams (Fig. 5) shows the reduced range of temperatures of the inflowing streams, consistent with their groundwater source. At site F for example, the range in temperatures was only 2.5°C, compared to 14.5°C in the lake.

Consequently, the tarn was warmer than the inflowing streams in summer but cooler in winter. The input of cold groundwater in summer may explain why the surface water temperature was cooler than expected from elevation alone. Based purely on their seasonal temperature variation, sites B, C, E and F appear to be largely groundwater-fed.

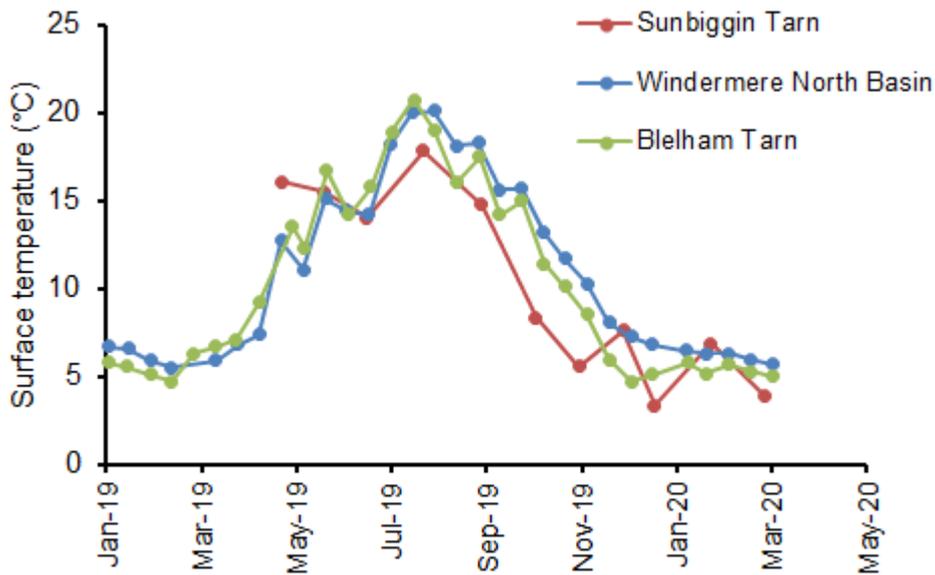


Figure 4. Seasonal changes in surface water temperature in Sunbiggin Tarn in comparison to two nearby lakes in the English Lake District. The data from Sunbiggin Tarn were measured at the shore apart from in July when they were measured at the centre of the lake, the data from the two other lakes were measured at the centre of each lake (data from UKCEH).

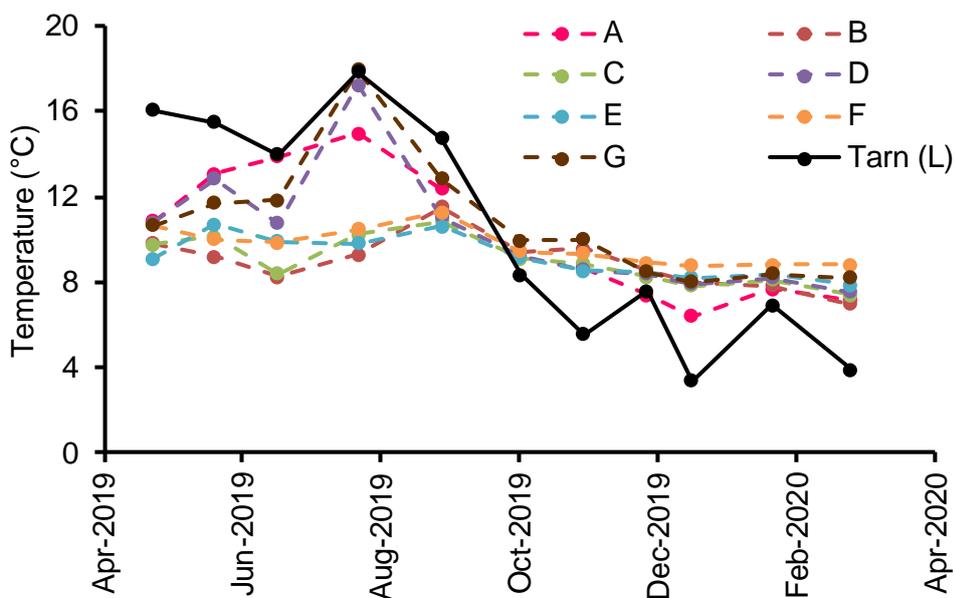


Figure 5. Seasonal changes of water temperature at the surface of Sunbiggin Tarn and the studied inflowing streams. See Fig. 3 for site locations.

Conductivity, pH and alkalinity

Conductivity is a measure of the total ionic concentration of water and in this Karst landscape will largely reflect the ions resulting from the dissolution of limestone in the catchment.

Alkalinity was only measured in the Tarn, however based on the data collected here, there is a reasonably good relationship between conductivity and alkalinity (Fig. 6) and so alkalinity in the flowing streams was estimated from conductivity:

$$\text{Alkalinity (mequiv L}^{-1}\text{)} = 0.0086 * \text{conductivity (}\mu\text{S cm}^{-1}\text{)} + 0.1012, R^2 = 0.919 \quad (\text{Equn 1})$$

Calcium concentrations were estimated from measurements of concentration of calcium and alkalinity from the Tarn in Carrick & Sutcliffe (1982):

$$[\text{Ca}^{2+}] \text{ (mmol L}^{-1}\text{)} = 0.5574 * \text{Alkalinity (mequiv L}^{-1}\text{)} - 0.1621, R^2 = 0.977 \quad (\text{Equn 2})$$

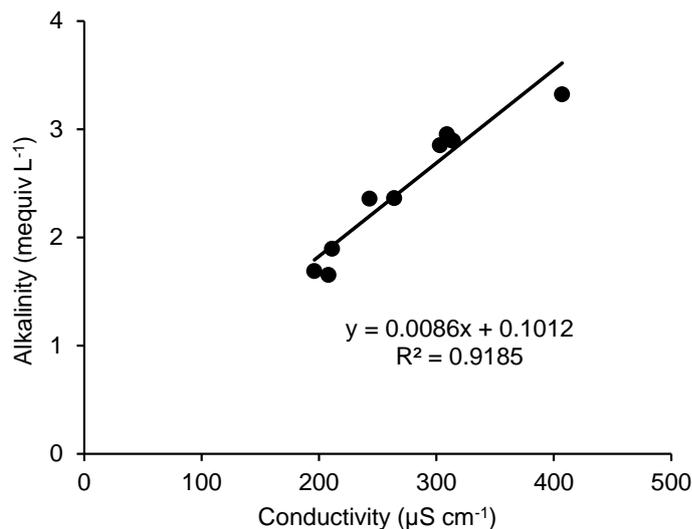


Figure 6. Linear regression between alkalinity and conductivity in Sunbiggin Tarn.

These relationships reflect the dominance of calcium carbonate in the ionic composition of Sunbiggin Tarn.

The pH in the tarn was mainly above pH 8 and normally higher than in the inflowing streams (Fig. 7). In contrast, conductivity and alkalinity were lower in the tarn than in the inflowing streams, which is consistent with substantial precipitation of calcite during the summer growing season. The inflowing streams had high CO_2 concentration of on average between 0.106 and 0.188 mmol L^{-1} which is consistent with a substantial groundwater input, while the tarn had a lower average CO_2 concentration of 0.055 mmol L^{-1} (Table 4). The streams were oversaturated with CO_2 by on average 4.7- to 8.6-times while the tarn was only 2.5- times oversaturated with CO_2 . Both streams and tarn will be a source of CO_2 to the atmosphere and the lower CO_2

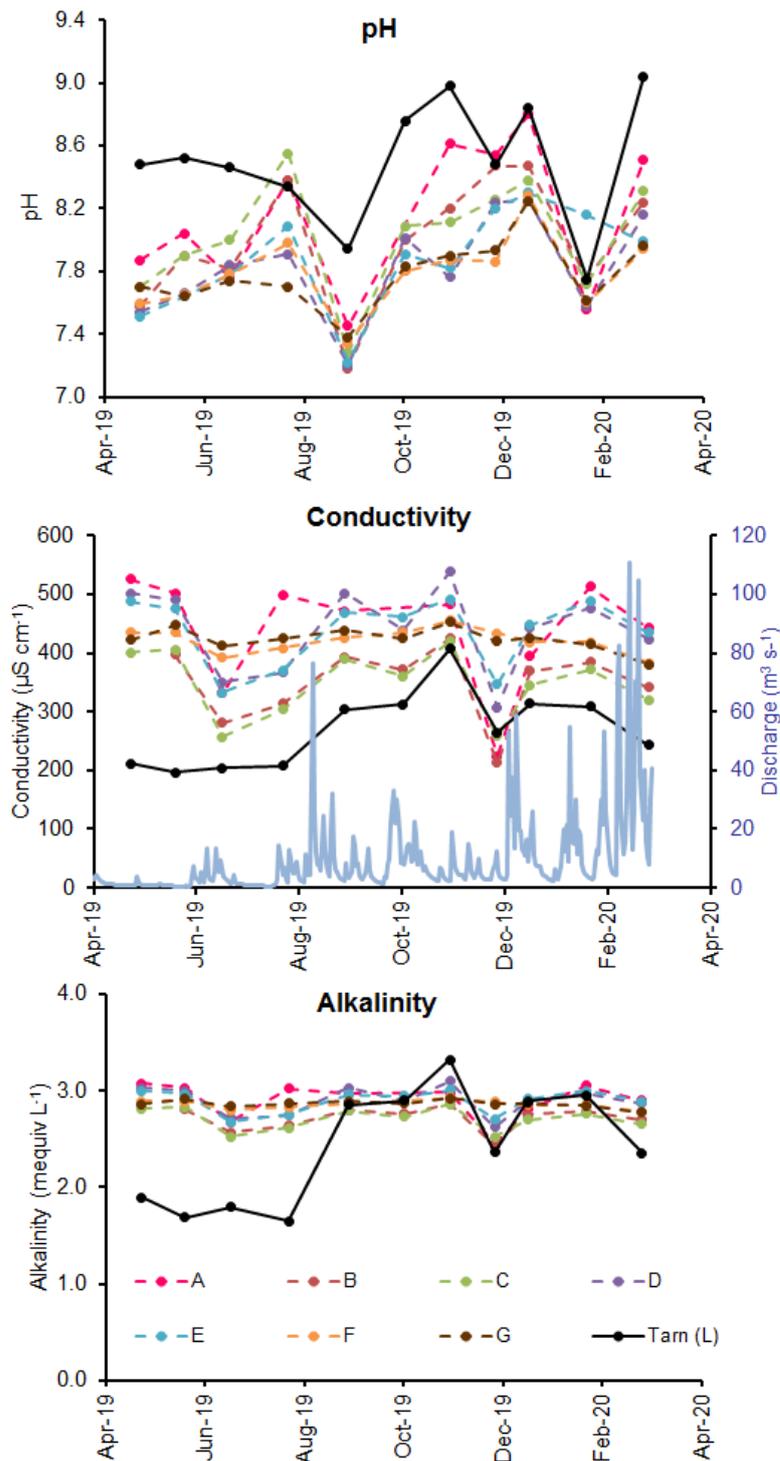


Figure 7. Changes in pH, conductivity and alkalinity in the inflowing streams and Sunbiggin Tarn. Alkalinity was measured for the Tarn but estimated from conductivity for the streams using equn 1. Daily average discharge is shown for Lunes Bridge on the River Lune. See Fig. 3 for site locations

concentrations in the tarn will have resulted from uptake by net primary production and CO_2 loss at the tarn surface. On average, calculations suggest that all the streams and the tarn were

Table 4. Average carbonate chemistry at the seven measured inflowing streams and the tarn. In the streams, alkalinity is estimated from conductivity. C_T , CO_2 , HCO_3^- and CO_3^{2-} are total inorganic carbon, carbon dioxide, bicarbonate and carbonate, respectively.

Site	Alkalinity (mequiv L ⁻¹)	C_T (mmol L ⁻¹)	CO_2 (mmol L ⁻¹)	HCO_3^- (mmol L ⁻¹)	CO_3^{2-} (mmol L ⁻¹)	CO_2 over-saturation (ratio)	Calcite saturation index
A	4.092	4.146	0.113	3.974	0.058	5.2	5.1
B	3.243	3.330	0.116	3.185	0.029	5.1	2.0
C	3.186	3.263	0.106	3.130	0.028	4.7	1.9
D	4.010	4.175	0.188	3.966	0.022	8.6	2.0
E	3.949	4.093	0.168	3.901	0.024	7.5	2.2
F	3.731	3.870	0.159	3.692	0.019	7.2	1.6
G	3.763	3.899	0.155	3.725	0.019	7.2	1.7
Tarn	2.425	2.448	0.055	2.362	0.031	2.5	1.5

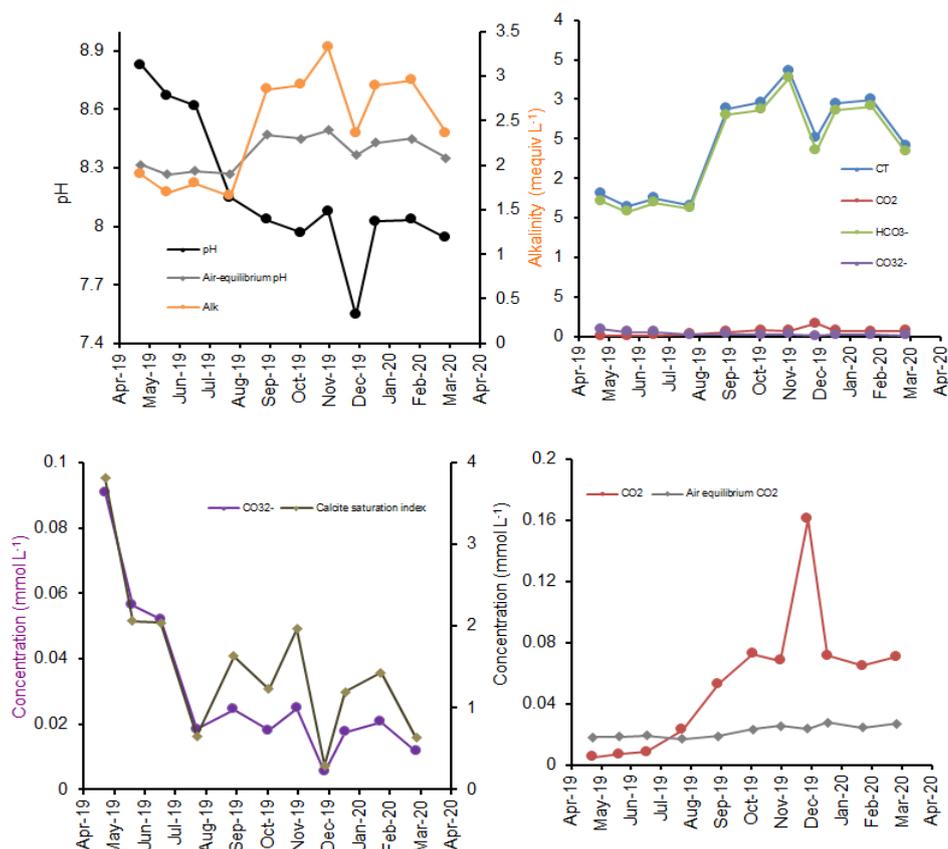


Figure 8. Seasonal patterns of pH, alkalinity and carbonate chemistry in Sunbiggin Tarn. C_T , CO_2 , HCO_3^- and CO_3^{2-} are the concentrations of total inorganic carbon, carbon dioxide, bicarbonate and carbonate, respectively. Air-equilibrium values represent the temperature-dependent conditions if the tarn was in equilibrium with an atmospheric CO_2 partial pressure of 410 ppm. The calcite saturation index represents the product of calcite and carbonate divided by the calcite solubility product: values less than one indicate calcite undersaturation and values over one, oversaturation.

also oversaturated with respect to the solubility product of calcite and there would therefore be a tendency for calcite to precipitate (Table 4). The tufa around some springs in the catchment (Holdgate, 1950) will be formed by this mechanism.

More detailed measurements and calculations for the tarn, presented in Fig. 8, show that CO₂ is undersaturated during the growing season, very likely as a result of uptake of CO₂ and/or HCO₃⁻ by phytoplankton and macrophytes, but also evasion of CO₂ to the atmosphere. During these periods of elevated pH and CO₃²⁻ concentration the calcite solubility index was markedly above 1 so that calcite precipitation is likely to have taken place. Based on the alkalinity, this appears to have taken place before the first sampling date at the end of April 2019.

Seasonal changes in nutrient concentrations

Within the tarn, concentrations of TP varied between 4 and 29 µg L⁻¹ and concentrations of TN varied between 330 and 660 µg L⁻¹. Median value of TP and TN were 11 and 390 µg L⁻¹ respectively. The median concentration of TP in the streams varied between 4 and 102 µg L⁻¹ which is both lower and higher than that in the tarn (Fig. 9). In contrast, the concentrations of

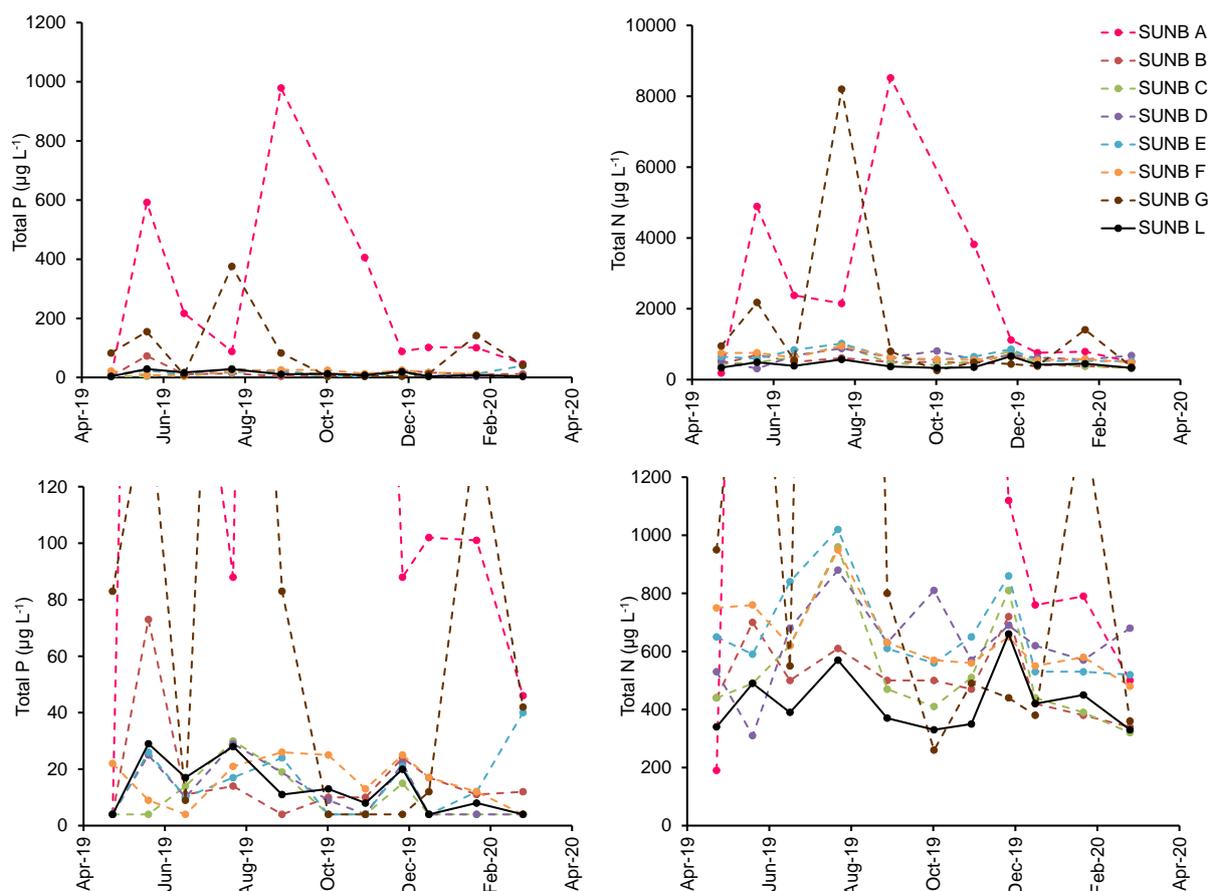


Figure 9. Seasonal change in concentration of total phosphorus (left-hand columns) and total nitrogen (right-hand columns). The lower two panels show the same data on an expanded scale.

TN in the streams was generally much higher than in the tarn with median concentrations varying between 470 and 1635 $\mu\text{g L}^{-1}$. Two of the smallest streams, A and G had some of the highest TP and TN concentrations which could be related to small particles in the water sample, despite filtering through a coarse filter during collection, although some of these particles probably enter the tarn during periods of high rainfall and flow. Concentrations of TP in May, June and July were slightly higher than at other times of year which could result from internal loading, but the lack of regular depth-profiles make this uncertain.

Approximate estimation of relative nutrient load from the inflowing streams

Estimating nutrient load from streams to standing waters is inherently difficult to do and especially so at Sunbiggin Tarn because of the complicated hydrology and because some of streams A, F and G, were too small and shallow to measure flow. Interpreting these rough estimates are complicated further by the single measurement of flow and, with respect to load from the streams to the tarn, the unknown contribution of groundwater inputs. Nevertheless, a first attempt to estimate the relative contribution of the different streams to the load of TP and TN has been made using data from streams B to E that together comprise ~90% of the catchment area (Table 5) The product of the median concentrations of each nutrient and the proportion of the measured flow was calculated to estimate relative load. The estimates (Table 6) show that stream A has the highest median concentration of TN and TP but this could be caused in part by the high particulate density in the very small stream (Appendix A). Stream E contributed the largest percent of the TP load and streams D and E the largest percent of the TN load. However, these were also the largest sub-catchments and stream B had the largest contribution of TP and TN in proportion to its sub-catchment area. It could be relevant that there has been a large death of heather in the sub-catchment of stream B (and elsewhere) caused by the heather beetle.

Table 5. Flow measurements at four of the inflowing streams on 31/10/2019 at Sunbiggin Tarn. See Fig. 3 for site location.

Site	Discharge ($\text{m}^3 \text{s}^{-1}$)	Proportion of total measured discharge	Catchment proportion [†]
A	-	-	-
B	0.0025	0.125	0.02
C	0.0054	0.269	0.10
D	0.0060	0.299	0.39
E	0.0062	0.307	0.39
F	-	-	-
G	-	-	-
TOTAL	0.0201	1.00	0.90

*Flow too low to measure at sites A, F and G.

[†] Estimated from the UKCEH Flood Estimation Handbook.

Table 6. Median concentrations of total phosphorus and total nitrogen and estimates in the different streams of their load based on flow measurements in Table 5, and load weighted by sub-catchment area. The highest value in each column is underlined and bold.

Stream	Median [TP] ($\mu\text{g L}^{-1}$)	Median [TN] ($\mu\text{g L}^{-1}$)	% TP load	% TN load	%TP load/ % sub-catchment area	%TN load/ % sub-catchment area
A	<u>102</u>	<u>1635</u>	-	-	-	-
B	11	500	17.0	11.0	<u>8.5</u>	<u>5.5</u>
C	4	470	13.3	22.4	1.3	2.2
D	6.5	630	24.1	<u>33.4</u>	0.62	0.86
E	12	610	<u>45.6</u>	33.1	1.2	0.85
F	17	620	-	-	-	-
G	42	550	-	-	-	-
Tarn	11	390	-	-	-	-

Phytoplankton

This work was carried out as a supplement to the contracted work. The photosynthesis pigment chlorophyll *a*, is commonly used to quantify phytoplankton abundance. Using this measure, the maximum phytoplankton abundance, at $9.6 \mu\text{g L}^{-1}$, was measured at the end of August 2019 (Fig. 10). This is considerably lower than the value measured by the Environment Agency in the same month between 2004 and 2006 at over $40 \mu\text{g L}^{-1}$ (Fig. 2). The annual average and median chlorophyll *a* concentration were 3.4 and $2.6 \mu\text{g L}^{-1}$ respectively. These are lower than average and median values in another marl lake, Malham Tarn between 1985 and 1987 at 7.1 and $5.0 \mu\text{g L}^{-1}$ respectively (Talling & Parker, 2002) and median concentrations measured by the Environment Agency at Sunbiggin Tarn between 2004 and 2006 at $8.1 \mu\text{g L}^{-1}$. The summer phytoplankton in Sunbiggin Tarn comprises a diverse mix of different taxa and phyla (Table 7). Although we did not measure biovolume of the different taxa, two motile species, the dinoflagellate *Ceratium hirundinella* and the cryptophyte *Rhodomonas* sp., were probably dominant. Diatom numbers appeared low which is unsurprising given the low SiO_2 concentrations recorded by the Environment Agency in previous years between February and September (Fig. 2), probably related to the predominantly limestone catchment. Cyanobacteria (blue-green algae) were noticeable by their almost complete absence. The broad phytoplankton composition is comparable to that recorded in another marl lake, Malham Tarn (Talling & Parker, 2002).

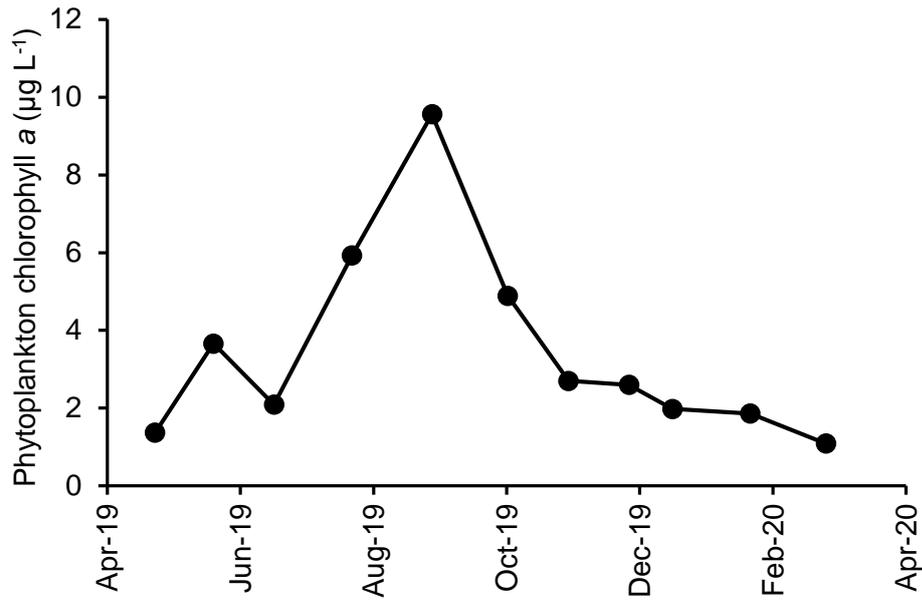


Fig. 10. Seasonal phytoplankton chlorophyll a concentration. Samples were collected from the edge of the lake (Fig. 3) apart from the sample at the end of July that was from the open water during the depth-profile measurements.

Table 7. Species composition and density of phytoplankton at Sunbiggin Tarn. The water derived from an integrated sample of the top 5 m collected from the centre of the tarn on 23 July 2020.

Taxon	Form	Algal group	unit mL ⁻¹
<i>Chroomonas</i> sp.	CELL	Chrysophyte	14.3
<i>Mallomonas akrokomas</i>	CELL	Chrysophyte	9.5
<i>Mallomonas</i> sp.	CELL	Chrysophyte	0.3
<i>Uroglena</i> sp.	CELL	Chrysophyte	9.5
<i>Cryptomonas</i> sp.	CELL	Cryptophyte	39.4
<i>Rhodomonas</i> sp.	CELL	Cryptophyte	1087.6
Unidentified blue-green	CELL	Cyanobacterium	0.5
Unidentified blue-green	FILAMENT	Cyanobacterium	3.7
<i>Asterionella formosa</i>	CELL	Diatom	0.3
<i>Cyclotella</i> sp	CELL	Diatom	0.6
<i>Cymbella</i> sp.	CELL	Diatom	0.6
<i>Fragilaria capucina</i>	CELL	Diatom	3.4
<i>Fragilaria capucina</i>	FILAMENT	Diatom	1.6
<i>Nitzschia/ Synedra</i>	CELL	Diatom	1.2
<i>Pennate diatoms</i>	CELL	Diatom	0.6
<i>Synedra</i> sp.	CELL	Diatom	2.2
<i>Synedra ulna</i>	CELL	Diatom	0.6
<i>Synedra ulna</i>	DEAD	Diatom	0.3
Unidentified diatom	CELL	Diatom	23.9
<i>Ceratium hirundinella</i>	CELL	Dinoflagellate	9.0
<i>Ceratium hirundinella</i>	DEAD	Dinoflagellate	0.3
<i>Gymnodinium</i> sp.	CELL	Dinoflagellate	0.3
<i>Peridinium</i> sp.	CELL	Dinoflagellate	0.3
<i>Ankyra judayi</i>	CELL	Green alga	19.1
<i>Asterococcus</i> spp.	CELL	Green alga	1.2
<i>Chlamydomonas</i> sp.	CELL	Green alga	4.8
<i>Chlorella</i> sp.	CELL	Green alga	47.7
<i>Closterium</i> spp.	CELL	Green alga	0.3
<i>Coenochloris</i> sp.	CELL	Green alga	33.5
<i>Coenochloris</i> sp.	COLONY	Green alga	2.5
<i>Cosmarium humile</i>	CELL	Green alga	0.3
<i>Crucigeniella irregularis</i>	CELL	Green alga	3.1
<i>Crucigeniella irregularis</i>	COLONY	Green alga	0.3
<i>Elakatothrix</i> sp.	CELL	Green alga	0.9
<i>Elakatothrix</i> sp.	COLO	Green alga	0.3
<i>Oocystis</i> sp.	CELL	Green alga	3.4
<i>Pandorina morum</i>	CELL	Green alga	5.0
<i>Pandorina morum</i>	COLONY	Green alga	0.3
<i>Staurastrum cingulum</i>	CELL	Green alga	0.3
<i>Tetraspora lemmermannii</i>	CELL	Green alga	331.6
<i>Tetraspora lemmermannii</i>	COLONY	Green alga	4.0
<i>Ulothrix/ Geminella</i>	CELL	Green alga	2.2
<i>Ulothrix/ Geminella</i>	FILAMENT	Green alga	0.9
Unidentified cell	CELL	-	2.8

Depth profiles at the centre of the lake

On the 23rd July 2019, depth profiles were measured at the centre of the Tarn when the lake depth was 9.2 m (see Fig. 3 for location). The Secchi depth was 3.2 m. Using the rough relationship that the depth of the 1% subsurface light, roughly representing the bottom of the euphotic zone is $3.19 \times$ Secchi depth, the bottom of the euphotic zone was estimated to be at 10.2 m, more than the maximum depth at the time of sampling of 9.2 m. Macrophyte light requirements are substantially greater than this. Using the relationships in Middleboe & Markager (1997), a Secchi depth of 3.2 m, assuming it is reasonably constant seasonally, would yield a maximum colonised depth of about 4.4 m for elodeid macrophytes and 4.7 m for charophytes. This might represent poor light conditions given that the measurement was made when the phytoplankton chlorophyll *a* concentration was the second-highest of the monthly samples although the Secchi depth was deeper than the 2.2 m recorded on 13 August 2002 (Goldsmith et al. 2003) but very similar to the depth reported in Pentecost (2013) at 3.1 m on 4 June 2013. Nevertheless, these estimated macrophyte depth limits are substantially less than those for a clear marl lake in Sutherland, Loch Borrallie, where elodeid macrophytes reach 6.5 m and charophytes reach 15 m (Spence 1982). Indeed, Goldsmith et al. (2003) noted depth limits of only 1.4 m in a survey from 1982 and 2.5 m in a survey in 2002. Whether or not there has been an increase of macrophyte depth limits more recently is not known.

On the sampling date, the tarn was moderately stratified with a temperature difference of 6.1°C between the surface and bottom (Fig. 11). This is similar to the profile measured in June 2013 by Pentecost (2013) where the temperature difference was 6.0°C. The extent of stratification is slightly less than in a lake such as Esthwaite Water with a slightly greater maximum depth of 14 m where typically the summer top-bottom temperature difference is around 9°C reflecting the exposed site at Sunbiggin Tarn. The oxygen concentration was below saturation throughout the water column, possibly linked to input of groundwater with low oxygen concentrations. Oxygen concentrations fell to about 1% of air-saturation in the lower 1.5 m, equivalent to 0.12 mg O₂ L⁻¹ (Fig. 11). This concentration is lower than that recorded by Pentecost (2013) at 8 m, at about 6.5 mg L⁻¹, but this profile was taken earlier in the year (4 June 2013) and oxygen depletion at depth increases during the stratified period. Conductivity and SRP were measured on discrete water samples collected at five depths. Both increased with depth (Fig. 12) and the water collected from 8.5 m (close to the sediment) had a very high SRP concentration of 298 µg L⁻¹. We do not have depth profiles of pH and alkalinity, but assuming that, as in the surface waters, alkalinity is the major contributor to conductivity the same relationship (Equn 1) was used to estimate an alkalinity profile, shown graphically in Fig. 6. This calculation shows that there is a large increase of alkalinity in the hypolimnion (Fig. 12).

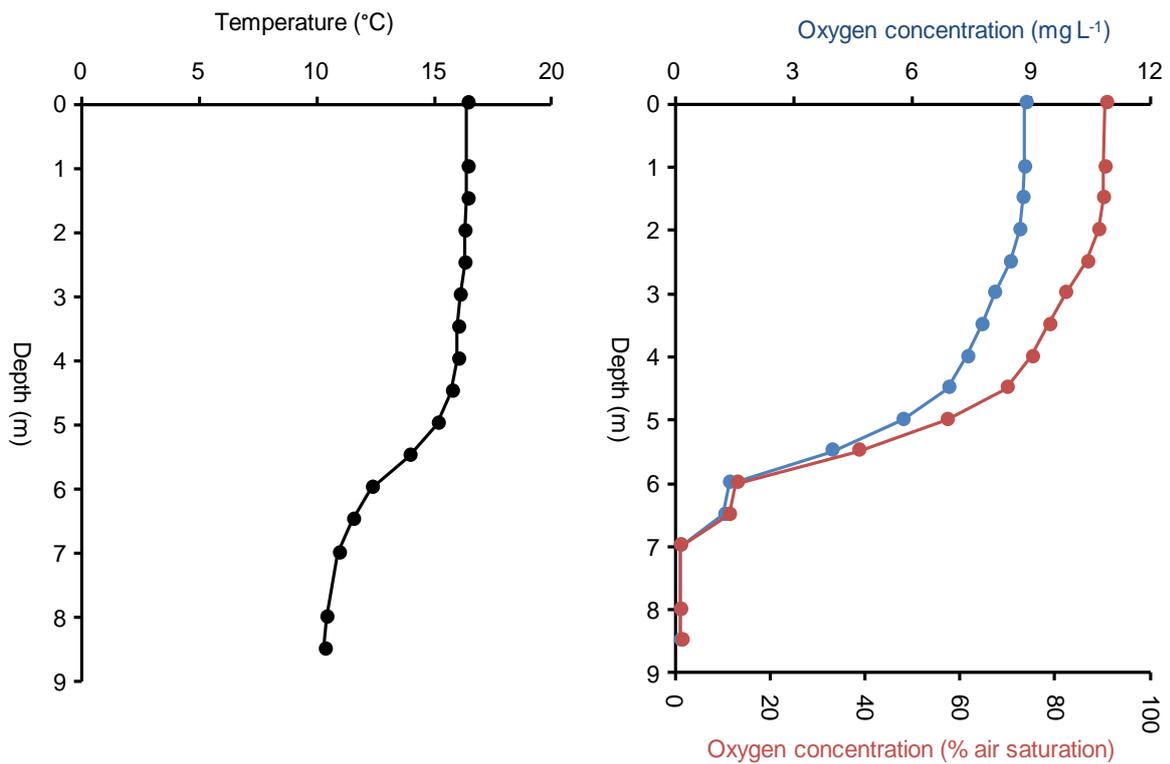


Figure 11. Depth profiles of temperature and oxygen concentration measured at Sunbiggin Tarn on 23/07/2019. The maximum depth at the time of sampling was 9.2 m.

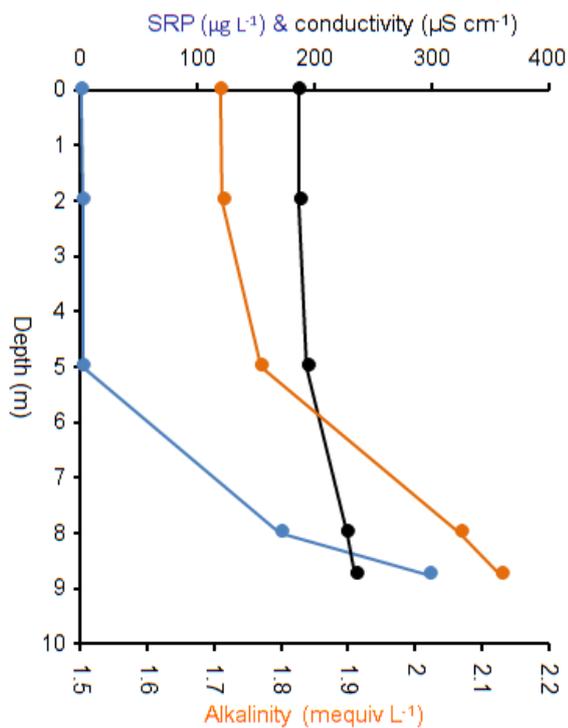


Figure 12. Depth profiles of Soluble Reactive Phosphorus (SRP), conductivity and calculated alkalinity at Sunbiggin Tarn on 23/07/2019. The maximum depth at the time of sampling was 9.2 m.

At least two mechanisms could be responsible for the high concentration of SRP at depth. First, the oxygen concentration at depth is low enough that the sediment surface might be anoxic, allowing ferric (Fe^{3+})-bound phosphate to be released into the water column as ferric iron become reduced to ferrous (Fe^{2+}) iron that does not bind phosphate (Mortimer 1941, 1942). A second mechanism of phosphate release at depth could result from apatite dissolution, releasing the phosphate that co-precipitated with calcite. Although both processes are independent, and both could be occurring simultaneously, they are linked since respiration at depth will deplete oxygen but will also generate CO_2 , reducing pH and leading to calcite becoming soluble.

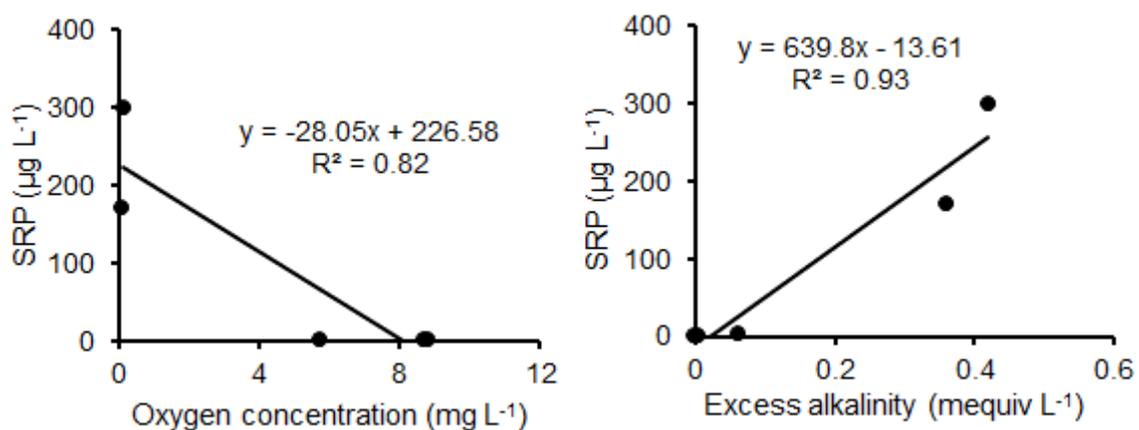


Figure 13. Relationships between SRP and oxygen concentration and SRP and excess alkalinity. Samples derived from depth profiles at Sunbiggin Tarn collected on 23/07/2019. Excess alkalinity is the additional alkalinity compared to the value at 0 m ($1.709 \text{ mequiv L}^{-1}$).

These two possibilities are explored in Fig. 13. There are significant correlations between SRP concentration and oxygen concentration ($P < 0.05$) and also excess alkalinity ($P < 0.01$) although the small number of data points is small, both processes are potentially occurring. The processes involved in phosphate precipitation and adsorption during calcite formation are complex and depend on a number of factors including phosphate concentration (Danen-Louwerse et al. 1995; Hartley et al. 1995). The release of phosphate from the sediment following dissolution is also complex and depends in part on the iron concentration (Golterman 2001). Nevertheless, as a rough calculation, different values of possible phosphorus incorporation into calcite were used. Danen-Louwerse et al. (1995) reported values of between 2.7 and $7.2 \text{ mg P g}^{-1} \text{ Ca}$ in lab experiments; Hamilton et al. (2009) found values between 0.49 and $2.62 \text{ mg P g}^{-1} \text{ Ca}$ in lake mesocosms, and Pentecost (2009, 2013) made direct measurements of the content of phosphorus in calcite from Sunbiggin Tarn and from the sediment with values of 0.58 and $2.35 \text{ mg P g}^{-1} \text{ Ca}$ respectively. Based on a SRP concentration at the deepest part of the depth-profile of $298 \mu\text{g L}^{-1}$, an 'excess alkalinity' there of $0.42 \text{ mequiv L}^{-1}$, the calculated concentration of SRP

estimated from calcite dissolution range between about 1% and 20% of the measured SRP concentration. The data from the tarn sediment (Pentecost 2009), although covering a range of years, probably represents the best estimate of the extent to which apatite dissolution can explain the measured SRP at depth, and this suggests the value is only 7%. These calculations therefore suggest that processes in addition to dissolution of calcite/apatite are responsible for the high SRP concentrations at depth, but the single depth-profile and limited variables measured (such as direct alkalinity, pH and calcium) limits further interpretation.

CONCLUSIONS

The conclusions in this report are specifically structured around the questions that were posed in the original documentation.

Whether marl formation is likely to be occurring within the lake

Sunbiggin Tarn is a marl lake and there are different lines of evidence that marl forms during the summer growing season. First, alkalinity in the tarn between April and July is substantially lower than between the end of August and February (Fig. 7). Secondly, alkalinity is also substantially lower than the alkalinity of the inflowing streams between April and July but very similar to the streams later in the year when tarn pH is lower. Thirdly, calculations show that the calcite saturation index was above 2 (indicating that calcite was highly oversaturated) in the summer but undersaturated or only slightly oversaturated at other times of the year. Slight oversaturation (ie a saturation index >1) does not necessarily lead to calcite precipitation in the absence of nucleation sites (Hartley et al. 1995). Finally, dissolved calcium in Sunbiggin Tarn in the summer growing season is nearly half that in the winter based on Environment Agency data between 2004 and 2006 (see Fig. 4 in Pentecost 2013). It is unclear whether the precipitation is occurring within the lake surface or on the surface of charophytes or other macrophytes at depth. Both are possible and further work involving more frequent depth profiles would be needed to resolve this. The current data and calculations suggest that anoxia-triggered release of phosphorus is likely to be more important than release of phosphorus from apatite dissolution at depth in explaining the high concentrations of soluble reactive phosphorus measured at the bottom of the tarn.

Whether there is a summer increase in TP indicative of internal loading

Since Sunbiggin Tarn is stratified for at least part of the summer, one would only expect to see an increase of TP derived from internal loading when stratification broke down. With monthly monitoring it is possible that this 'pulse' might be missed, especially if it coincided with high flow: the data in Fig. 9 did not reveal an obvious pulse. However, the depth profiles show that high concentrations of SRP are present at the bottom of the lake when it is stratified (Fig. 12). Without bathymetric information and more frequent depth-profiles, it is not possible to quantify the magnitude of the effect this will have when mixed into the whole water column (i.e. it is a high concentration but, depending on the relative water volumes, it could be a small amount) and the ecological effect might also be limited if mixing occurs at the end of the growing season when phytoplankton growth will start to become limited by light and

temperature. First order calculations suggest that dissolution of calcite/apatite is probably a minor component of the different process producing the high SRP concentrations at depth. It is also unknown whether Sunbiggin Tarn is polymictic, with regular formation and breaking down of stratification during the summer, in which case there could be multiple pulses of SRP, or whether stratification is stable during the summer so inputs of phosphorus largely occur when stratification breaks down at the end of the season. Since the mean depth is only about 4 m, half of the lake area might be too shallow to be strongly stratified. This could mean that these sediments do not experience low oxygen concentrations/ low pH to trigger release of phosphorus from the sediment, although they would be susceptible to wind- and wave-induced disturbance of the sediment releasing phosphate from interstitial water. Furthermore, high pH (that could be produced by macrophyte photosynthesis can also lead to the release of ferric-bound phosphate from the sediment (Drake & Heaney 1987).

Whether the lake is responding to external as opposed to internal loads

Some of the discussion above is also relevant to this question. Similar to the caveat about knowing bathymetry to estimate the quantitative importance of the high SRP at depth, estimating the importance of the TP in inflowing streams requires flow to be known so that load can be estimated. This is very difficult in many of the streams when flow is very low and the hydrological situation is complicated because of the unknown, but strongly suspected, groundwater input. Table 6 shows that the median TP concentration in the tarn is lower than in three of the measured inflows, the same as one, and greater than two of the streams so it is possible that lake TP concentrations can be accounted for by stream inflow. This suggests that external load is largely or wholly controlling TP concentration; but the lack of good hydrological measurements make this uncertain. Of the different streams, stream D (Fig. 3) appears to make the greatest contribution to TP load while stream B (Fig. 3) has a disproportionately large load taking its estimated catchment area into account (Table 6). If the same calculations are performed for TN then the lake has markedly lower median concentrations than any of the monitored streams (Table 6) suggesting a large loss process such as denitrification or nitrogen uptake within the tarn. A similar pattern of N-loss was recorded in another marl lake, Malham Tarn (Talling & Parker, 2002). Streams D and E are major sources of TN to the tarn and again stream B has the highest input considering its estimated catchment area.

Whether the lake nutrient concentration is moving in the right direction, has it declined since previous reports and is it approaching the target

A caveat with the following is that the different analyses were performed by different labs and more importantly the water samples may have been collected from different locations (near-shore, open water, outflow for example). In the analysis below, the data are taken at face value. Pentecost (2013) measured TP on some of the inflow streams on two occasions. Based solely on these values the mean in 2013 was 36 compared to 26 $\mu\text{g L}^{-1}$ in 2019-2020 but given the variability in concentration (Fig. 9) it cannot be concluded that this necessarily represents a reduction in concentration.

Concentrations within the lake are less variable than concentrations in streams making comparisons more reliable. The comparison in Table 8 indicates that between 2003 and 2019-2020 there has possibly been a reduction in TP concentration in the tarn and possibly also TN although no data are available from the earliest time period. Phytoplankton chlorophyll *a* concentrations are lower than in 2004-2006 but slightly higher than those recorded in 2003. In 2003 Goldsmith et al. (2003) estimated that the phosphorus load to the tarn from a population of black-headed gulls (*Larus ridibundus*), that exceeded 12,000 breeding pairs, was of the order of 67.8 kg P y^{-1} . For a catchment area of 1.83 km^2 , an annual rainfall of 1.3 m and an evapotranspiration factor of 25 % (Table 1), the annual discharge through the tarn would be 1.784 Mm^3 . Dilution of the 67.8 kg P y^{-1} load from the gulls into this volume would produce a TP concentration of 38 $\mu\text{g L}^{-1}$, so the abrupt decline in black-headed gulls and their disappearance by 2005 (Holdgate 2016) is likely to be responsible, at least in part, for the observed reduction in TP concentration in the tarn.

Table 8. Comparison and median and mean concentrations ($\mu\text{g L}^{-1}$) of total phosphorus (TP), total nitrogen (TN) and phytoplankton chlorophyll *a* (Chl *a*) in Sinbiggin Tarn on three occasions.

Years	# samples	Median TP	Mean TP	Median TN	Mean TN	Median Chl <i>a</i>	Mean Chl <i>a</i>	Ref
2003	5	22.5	33.6	-	-	1.1	2.4	1
2004-2006	23-29	29.0	28.6	491	500	8.1	19.1	2
2019-2020	11	11.0	13.0	390	427	2.6	3.4	3
NE target		-	11.0	-	1500	-	7.0	4

1. Goldsmith et al. (2003); 2. Environment Agency; 3. This study, 4. Ruth Hall pers. comm..
 ‘-’ no data.

Whether there are visible signs of filamentous algal growth and how they fit with the water quality data collected

Filamentous green algae were visible in some of the inflowing streams on the first visit on 23 April 2019. Photographs taken at each sampling stream and date (Appendix 1) suggest that they were less abundant at other times of year. A BBE Moldaenke 'Algal Torch' that measures benthic chlorophyll by fluorescence was used on 17 June 2019, but very low chlorophyll values were recorded (data not presented).

Whether nitrogen concentrations are at levels that may inhibit charophyte growth (above 2 mg L⁻¹), or whether they are at levels that limit other algal growth

High concentrations of nitrogen are unlikely to inhibit charophyte growth directly. For example, *Chara hispida* was grown successfully in aquaria at nitrate concentrations of 8 to 10 mg N L⁻¹ (Rodrigo et al. 2007). On the other hand Lambert & Davy (2010) reported maximum growth rates in laboratory experiments at 0.5 mg N L⁻¹ and an IC₅₀ (the concentration at which the maximal growth rate was halved) at 5.6 mg N L⁻¹. However, high nitrogen concentrations are normally associated with high phosphorus concentrations and these together can produce eutrophic conditions leading to increased phytoplankton growth that could have an indirect effect on benthic plants such as charophytes via a reduction in light and potentially hypoxic or anoxic conditions at depth. Lambert & Davy (2010) recommended a maximum nitrate concentration of 2 mg N L⁻¹ based on an analysis of field data that will include competition and indirect effects. In either case, the maximum TON (largely nitrate) concentration recorded for Sunbiggin Tarn by the Environment Agency (Fig. 2) was about 0.55 mg N L⁻¹, well below any possible toxic concentration so negative effects of nitrate on the charophytes in Sunbiggin Tarn are unlikely.

It is possible, however, that nitrogen is limiting in the tarn though this needs to be checked. For average balanced growth of algae and plants, 16 mol of nitrogen are typically required for every mol of phosphorus (based on the Redfield ratio) so nitrogen is required in relatively large amounts. While the focus of inland waters eutrophication has been on phosphorus, there is a growing appreciation that nitrogen is an important nutrient that can control algal and plant growth (Moss et al. 1992; Maberly et al. 2002; Elser et al. 2007). In Sunbiggin Tarn (and also Malham Tarn, Talling & Parker 2002) concentrations of total nitrogen are below those of most of the inflowing streams (Fig. 9) and could potentially be limiting phytoplankton production, or be co-limiting with phosphorus. This is reinforced by the measurements of total oxidised nitrogen (nitrate plus nitrite) by the Environment Agency between 2004 and 2006 which were below the limit of detection of 0.2 mg N L⁻¹ in the summer although an even lower concentration of TON, 0.1 mg N L⁻¹, is sometimes used to indicate nitrogen limitation (Maberly et al. 2020).

Summary

Sunbiggin Tarn appears to be functioning like a typical marl lake with summer precipitation of calcite caused by inflow of water that is oversaturated with calcium carbonate and CO₂ and subsequent increases in pH as CO₂ evades to the atmosphere and (along with HCO₃⁻) is taken up during photosynthesis. This causes co-precipitation of calcite and phosphate, reducing phosphate concentrations in the water column. Based on a single depth profile, SRP concentrations are high at the bottom of the lake and this could result from redox-mediated release from the sediment caused by the low oxygen concentrations and dissolution of calcite/apatite inferred from the increase in alkalinity at depth (calculated from conductivity). The limited evidence available suggests that release from the sediment is more important.

Concentrations of TP within the lake are broadly consistent with concentrations in the inflowing streams but lack of flow data and the uncertain influence of groundwater inputs restricts further conclusions. Stream B towards the north-east part of the lake appears to have the largest input of TP and TN compared to its estimated sub-catchment area and this was also an area where heather was badly affected by heather beetle – but this link is conjectural. In contrast to TP, concentrations of TN in the inflowing streams exceed that in the tarn showing that nitrogen is being removed from the water by processes such as denitrification and uptake by the freshwater plants: *Chara* beds are known to have a major effect on nitrogen removal (Rodrigo et al. 2007) and other macrophytes are also able to remove nutrients from the water column. It is possible that the phytoplankton within the tarn are limited, or co-limited, by nitrogen rather than the more commonly considered nutrient, phosphorus. More work would be required to test this. Knowing the nutrients that control productivity is important for the production of robust management plans (Maberly et al. 2020).

There is some evidence that concentrations of TP in the tarn have declined since 2003 and this could be consistent with the loss of the large colony of black-headed gulls since 2005.

Phytoplankton chlorophyll *a* concentrations and species composition are typical of marl lakes.

During the period of this survey (April 2019 to February 2020) annual mean (noting one month was missing because of Covid restrictions) were below the targets set by Natural England for total nitrogen and phytoplankton chlorophyll *a*, but slightly above the target for total phosphorus (Table 8). Since the phytoplankton chlorophyll *a* and the concentration of TN is low, it is possible that the tarn is nitrogen-limited and the slight exceedance of the total phosphorus target is not a major cause for concern as it is not controlling water quality. Overall, further

monitoring is warranted to understand better the processes occurring in the tarn and its catchment and to ensure that the documented improvements continue (see section below).

RECOMMENDATIONS FOR FUTURE WORK

This report is based on a restricted set of variables in terms of determinands, temporal measurement frequency and limited depth-resolved data because of financial constraints. Although it provides broad answer to the questions posed in the original specification, it highlights areas where further research would allow greater clarity on how the tarn is operating.

Hydrology

A large uncertainty concerns the extent to which the tarn receives water from groundwater, but this is a difficult and expensive question to answer. From the point of view of managing the tarn, it would only be important if any groundwater inputs had concentrations of nutrients that were markedly different from the inflowing streams. This is possibly unlikely as the inorganic carbon chemistry of the streams themselves have a marked groundwater signature and many, such as site C, clearly derive directly from a spring. In view of this, we do not recommend attempting to determine groundwater inputs. *However, it could be useful to determine the total flow of water through the tarn at the outflow by installing a self-logging pressure sensor and determining discharge under a range of flow conditions.*

Bathymetry

An accurate bathymetry is not known. This knowledge would be useful in a number of areas including determining the water residence time more accurately, in combination with the hydrological measurements above, evaluating the consequence of the SRP concentrations in depth profiles in relation to internal P inputs to the surface water and identifying areas that could be colonised by macrophytes. *A survey based on echo-sounding, would be an efficient way to determine lake bathymetry and could also be used to provide broad distribution of macrophytes.*

Macrophyte species composition and distribution

The last published macrophyte survey was in 2002 and it did not provide detailed information on the areal- or depth-distribution of macrophytes, or their maximum depth limit. Macrophytes are an important part of the ecology and conservation value of this tarn and also markers for its ecological state. *In addition to the echo-sounding survey, underwater videos, shore inspection to determine a species list and transects and grapnel surveys using Site Condition Monitoring methods could be undertaken. The extent of any filamentous algae could be assessed during this survey.*

Seasonal and automatic monitoring and depth profiles

Many of the unresolved questions mentioned in this report turn on processes within the tarn itself, such as the unknown extent and duration of stratification, the concentrations of bio-available nutrients such as nitrate, ammonium and phosphate, the role of sediment release vs apatite dissolution in producing the measured high concentrations of SRP at depth. *A standard, ideally fortnightly, or failing that monthly, depth-resolved limnological survey should be carried out that includes measurements of temperature and oxygen, light climate, phytoplankton chlorophyll a, plant nutrients, alkalinity and inorganic carbon and calcium. An automatic monitoring buoy at the deepest point with a thermistor chain and simple meteorological instruments can be used to document changing stratification patterns at sub-hourly intervals to determine whether or not the lake is polymictic (with implications for internal nutrient loading). The extent of seasonal stratification should also be assessed at a littoral site.*

Nutrient limitation of phytoplankton

The available nutrient chemistry from the tarn, although limited, indicates that nitrogen or possibly nitrogen and phosphorus together (co-limitation) might control pelagic productivity in the tarn. *This question could be resolved by monthly nutrient bioassays of water samples incubated in the laboratory under controlled conditions and measuring phytoplankton growth following addition of different forms of nutrient.*

Sediment chemistry

Further information on sediment chemistry and its ability to bind or release phosphorus would help to evaluate whether anoxia or apatite dissolution are responsible for the elevated phosphate concentrations at depth. *Sediment cores collected from deep water could be incubated in the lab under controlled conditions of low oxygen and low CO₂ (to stimulate release of phosphate triggered by anoxia) or air levels of O₂ and high concentrations of CO₂ (to stimulate release of phosphate from apatite dissolution). Sediment traps at depth could be used to quantify the particulate flux of calcium and phosphorus to the sediment.*

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REFERENCES

- Bennion, H., Rawcliffe, R., Burgess, A., Clarke, G., Clarke, S., Davidson, T., Rose, C., Rose, N., Sayer C., & Turner S. (2009) Using novel palaeolimnological techniques to define lake conservation objectives. Report to Natural England.
- Carrick T.R. & Sutcliffe D.W. (1982). Concentrations of major ions in lakes and tarns of the English Lake District (1953 – 1978). Freshwater Biological Association. Occasional Publication No. 16.
- Danen-Louwerse H.J., Lijklema L. & Coenraats M. (1995). Coprecipitation of phosphate with calcium in Lake Veluwe. *Water Research* 29, 1781-1785.
- Drake J.C. & Heaney S.I. (1987). Occurrence of phosphorus and its potential remobilization in the littoral sediments of a productive English Lake. *Freshwater Biology* 17, 513-523.
- Lambert S.J. & Davy A.J. (2011). Water quality as a threat to aquatic plants: discriminating between the effects of nitrate, phosphate, boron and heavy metals on charophytes. *New Phytologist* 189, 1051-1059.
- Elser J.J., Bracken M.E.S., Cleland E.E., Gruner D.S., Harpole W.S., Hillebrand H., Ngai J.T., Seabloom E.W., Shurin J.B. & Smith J.E. (2007). Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine and terrestrial ecosystems. *Ecology Letters* 10, 1135-1142.
- Goldsmith, B.J., Luckes, S.J., Bennion, H., Carvalho, L., Hughes, M., Appleby, P.G. & Sayer, C.D. (2003). Feasibility studies on the restoration needs of four lake SSSIs. Report to English Nature
- Golterman, H.L. (2001). Phosphate release from anoxic sediment or 'What did Mortimer really write'. *Hydrobiologia* 450, 99-106.
- Hamilton S.K., Brusewitz D.A., Horst G.P., Weed D.B. & Sarnelle O. (2009). Bioogenic calcite-phosphorus precipitation as a negative feedback to lake eutrophication. *Canadian Journal of Fisheries and Aquatic Sciences* 66, 343-350.

- Hartley A.M., House W.A., Callow M.E. & Leadbeater B.S.C. (1995). The role of green algae in the precipitation of calcite and the coprecipitation of phosphate in freshwater. *Int. Rev. Ges. Hydrobiol.* 80, 385-401.
- Holdgate, M.W. (1955). The vegetation of some springs and wet flushed on Tarn Moor near Orton, Westmoreland. *Journal of Ecology* 43, 80-89.
- Holdgate, M. (2016). SunbigginTarn Notes on changes between 1950 and 2016.
- Layden A., Merchant C. & MacCallum S. (2015). Global climatology of surface water temperatures of large lakes by remote sensing. *International Journal of Climatology* 35: 4464–4479.
- Lund J.W.G., Kipling C. & LeCren E.D. (1958). The inverted microscope method of estimating algal numbers and the statistical basis of estimations by counting. *Hydrobiologia* 11, 143-170.
- Maberly S.C. (1996). Diel, episodic and seasonal changes in pH and concentrations of inorganic carbon in a productive English Lake, Esthwaite Water, Cumbria. *Freshwater Biology* 35, 579-58.
- Maberly S.C., King L., Dent M.M., Jones R.I. & Gibson C.E. (2002). Nutrient limitation of phytoplankton and periphyton growth in upland lakes. *Freshwater Biology* 47, 2136-2152.
- Maberly S.C., Pitt J.-A., Davies S. & Carvalho L. (2020). Nitrogen and phosphorus limitation and the management of small productive lakes. *Inland Waters* 10, 159-172.
- Mackereth, F.G.H., Heron, J. & Talling, J.F. (1978). *Water analysis: some revised methods for limnologists*. Freshwater Biological Association. Scientific Publication No. 36.
- McCormac M.M. (2003). The Upper Palaeozoic rocks and Quaternary deposits of the Shap and Penrith district, Cumbria (part of Sheet 30, England and Wales). British Geological Survey RR/01/10.
- Middleboe A. L. & Markager S. (1997). Depth limits and minimum light requirements of freshwater macrophytes. *Freshwater Biology* 37, 553-568.
- Mortimer, C. H. (1941). The exchange of dissolved substances between mud and water in lakes. *Journal of Ecology* 29, 280–329.
- Mortimer, C. H. (1942). The exchange of dissolved substances between mud and water in lakes. *Journal of Ecology* 30, 147–201.

- Moss B., McGowan S., Kilinc S. & Carvalho L. (1992). Current limnological condition of a group of the West Midland meres that bear SSSI status. Peterborough (UK): English Nature 320 p.
- Natural England (2013). National Character Area profile: 17: Orton Fells. NE 487.
- Otsuki A. & Wetzel R.G. (1972). Coprecipitation of phosphate with carbonates in a marl lake. *Limnology & Oceanography* 17, 763-767.
- Pentecost, A. (2009). The marl lakes of the British Isles. *Freshwater Reviews* 2, 167-197.
- Pentecost, A. (2013). A report on the current status of Sunbiggin Tarn, Cumbria with reference to the epiphytic algal flora, surface sediment chemistry and nutrient concentrations in the tarn and its feeder springs. Report to Natural England.
- Rodrigo M.A., Rojo C., Alvarez-Cobelas M. & Cirujano S. (2007). *Chara hispida* beds as a sink of nitrogen: evidence from growth, nitrogen uptake and decomposition. *Aquatic Botany* 87, 7-14.
- Spence D.H.N. (1982). The zonation of plants in freshwater lakes. *Advances in Ecological Research* 12, 37-125.
- Talling J.F. (1974). In standing waters. In: A Manual on Methods for Measuring Primary Production in Aquatic Ecosystems, Ed. R.A. Vollenweider (IBP Handbook No. 12, 2nd edn), pp. 119-123. Oxford, Blackwells.
- Talling J.F. & Parker J.E. (2002). Seasonal dynamics of phytoplankton and phytobenthos, and associated chemical interactions, in a shallow upland lake (Malham Tarn, northern England). *Hydrobiologia* 487, 167-181.

APPENDICES

Appendix 1. Photographs of the streams on each sampling location



SUNBIGGIN 23 APRIL 2019



SUNBIGGIN 20 MAY 2019





SUNBIGGIN 17 JUNE 2019





SUNBIGGIN 23 JULY 2019





SUNBIGGIN 29 AUGUST 2019





SUNBIGGIN 3 OCTOBER 2019





SUNBIGGIN 31 OCTOBER 2019



SUNBIGGIN 28 NOVEMBER 2019





SUNBIGGIN 18 DECEMBER 2019





SUNBIGGIN 23 JANUARY 2020





SUNBIGGIN 27 FEBRUARY 2020

