

PHOSPHORUS FRACTIONATION IN THE SEDIMENTS OF MALHAM TARN, NORTH YORKSHIRE

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ABSTRACT

Phosphorus fractionation studies were undertaken on five recent marls and one submerged peat sample from Malham Tarn. In the marls, the major fractions were oxide-adsorbed (mean 29% of total); reductant-soluble (24%) and residual (20%). Despite the high proportion of calcium carbonate in the sediments (72%), the carbonate phosphorus fraction was low (14%). Total phosphorus levels ranged from 2300 ppm at the sediment surface to ca 500 ppm at 70 cm depth and below. This recent increase in sediment total phosphorus appears to pre-date the Industrial Revolution and may be related to more intensive land management practices in the catchment over the past few hundred years.

INTRODUCTION

Malham Tarn is Britain's best known marl lake and, in common with the majority of our lakes, has undergone dramatic changes over the past few hundred years. The alkaline waters of the Tarn have provided an adequate buffer against the ravages of acid deposition, but the input of nutrients seems to have increased recently due to the intensification of farming and perhaps an increased human population density at the Field Studies Centre, situated above the north shore. The Tarn and its catchment contains a diverse and well studied biota (e.g. Bryce, 1962; Holmes, 1965). The floor of the Tarn is covered with extensive growths of *Chara* which provide shelter for a rich invertebrate fauna. It also precipitates significant quantities of calcium carbonate as marl (Pentecost, 1984), a process which appears to have continued in the Tarn for at least 10,000 years (Pigott & Pigott, 1959).

At the Malham Tarn Research Seminar held in November 1996, attention was drawn to the rapid changes currently occurring in the Tarn. The phytobenthos has recently switched from *Chara*-dominated to co-dominant *Chara-Elodea* (G. Hinton *in litt.*) and there is evidence of increased phytoplankton densities since the 1980s (author, unpublished). There is also a high probability of significant inputs of phosphorus from agricultural sources (Johnes, *in litt.*).

METHODS

Five samples of surface sediment were collected in 1-3 m water from Malham Tarn using a hand corer. Sample 1 was submerged peat from Tarn Moss while the remainder were *Chara* marls containing 60-80% calcium carbonate. Sample 5 was the least mineralised and was not associated with living *Chara*. In addition, an 80 cm piston core was obtained near the Tarn centre, consisting entirely of *Chara* marl (Fig. 1). All samples were bagged and stored at 4°C prior to analysis.

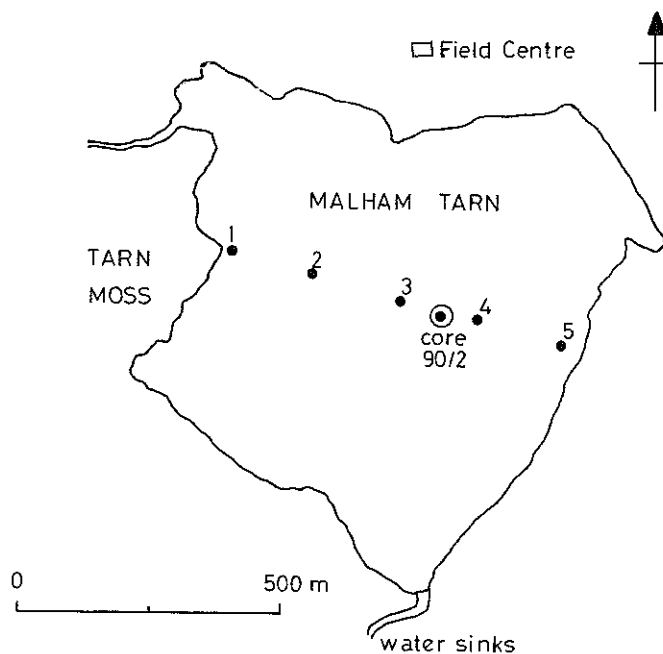


FIG. 1. Map of Malham Tarn showing the sediment sampling sites

Total reactive phosphate was determined on 1 g wet sediment which was dried at 105°C for 3 hours then thoroughly mixed and ground. A 250 mg sample was transferred to a flask with 2 ml 2 Normal hydrochloric acid added to remove carbonates, followed by 5 ml nitric acid. Samples were left overnight then evaporated to dryness. They were then transferred to 100 ml PTFE beakers with 2 ml 70% perchloric acid heated to 120°C and evaporated to dryness. A further 3 ml perchloric acid were added, evaporated again to dryness and the residue taken up into 1 ml 10N hydrochloric acid. After 2 hours, the solution was diluted to 50 ml and neutralised with sodium hydroxide using phenolphthalein as indicator. The samples were then analysed for reactive phosphate with the molybdenum blue method (Eisenreich *et al.*, 1975).

Phosphorus fractionation studies were performed only on the surface sediments. These were air-dried at 40°C, then two replicates of each sample were analysed using the method of Psenner *et al.* (1988). Sample replication was good (+10%). The calcium carbonate, acid insoluble and organic fractions of the sediments were obtained by thermal analysis.

RESULTS

Total phosphate levels in the piston core are shown in Fig. 2. Total phosphorus declines with sediment depth, falling from ca 3000 ppm (parts per million) at the surface to about 200 ppm (dry wt) in the oldest marls ($r = -0.635$, $p < 0.002$). There is considerable variation in the phosphorus levels with a trend toward increasing phosphorus in the younger sediments. A sample of *Chara globularis*, the principal marl-former in the Tarn, was also analysed and found to contain less phosphate than the sediment (Table 1, Fig. 2). The surface marls contained 720-3900 ppm total phosphorus (mean 2540 ppm) and there was no systematic variation along the sampling transect. The submerged peat sample of Tarn Moss contained less phosphorus (1290 ppm) than the marls.

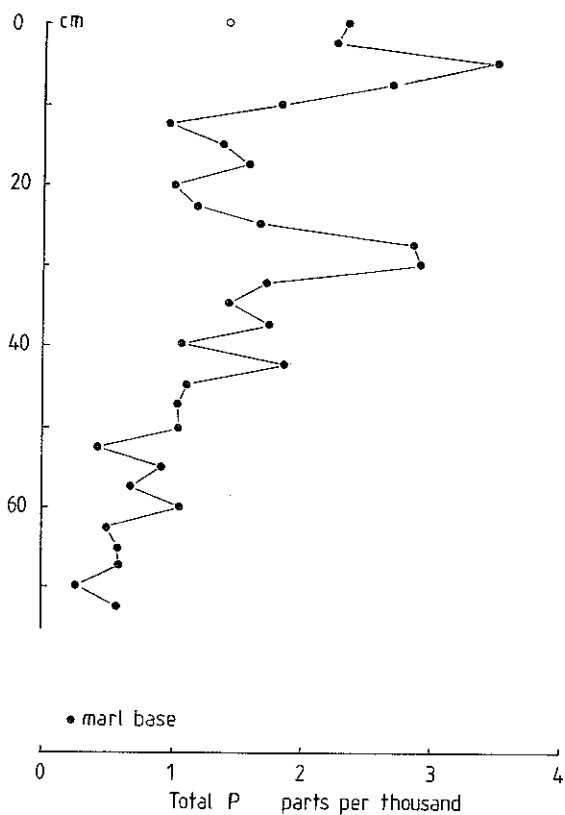


FIG. 2 Total phosphate in core 90/2, Malham Tarn (ppt dry wt.). Samples were analysed at 2.5 cm intervals. The open circle represents a modern sample of *Chara globularis*, the major marl-former.

TABLE 1. Phosphate fractions (ppm) and surface sediment composition (%) in core 90/2, Malham Tarn

Sample no.	NH ₄ extractable	di-thionite extractable	NaOH sorbed	NaOH organic	HCL extractable	Residual P	Total P	CaCO ₃ %	Organic matter %	Insol. matter %
1	79	38	380	10	98	680	1290	14.7	84.2	1.1
2	84	490	610	220	340	690	2430	62.9	19.4	17.7
3	360	840	1230	nd	360	510	3300	75.7	17.9	6.4
4	250	1640	810	300	380	560	3900	72.9	17.9	9.2
5	30	17	150	11	270	240	720	75.3	3.6	21.1
Core 90/2							2300			
<i>Chara</i>							1430			
mean	181	597	700	128	338	500	2588	71.7	14.7	13.6

Results of the fractionation studies are shown in Table 1 and Fig. 3. The ammonia-extractable phosphate represents the 'labile' or desorbed phosphorus and is not a significant fraction, usually less than 10% of the whole and there was no correlation with the organic matter content of the sediments. Buffered dithionite-extractable phosphorus is thought to correspond to the phosphorus released to lake water under anoxic conditions. Levels are particularly high in samples 2-4 associated with *Chara* where they constitute up to 40% of the total phosphorus. Alkali-extractable phosphorus can be divided into two forms: a) extractable phosphorus bound to oxides and exchangeable against OH⁻ - a significant fraction in all of the samples (20-30% of the total) and b) base-soluble organically-bound phosphorus which is a minor component, even in the peat. The hydrochloric acid-soluble fraction includes phosphate largely associated with the carbonates, a major sediment component of the marls. It was not, however, the dominant component and was most prevalent in the most mineralised marl sample no. 5 where it reached almost 40% of the total. Finally the unreactive, 'residual phosphorus' was found in all sediments, especially the peat where it may exist as recalcitrant organic species. It was a variable but significant fraction in the marls.

Several correlations were made between the fractions or their combinations and sediment composition. The only significant correlation was found between hydrochloric acid-extractable phosphorus and the calcium carbonate content ($r = +0.903$, $p < 0.05$). A weaker correlation was found between dithionite-extractable phosphorus and the organic matter content ($r = +0.658$, $p > 0.05$), excluding the peat sample.

DISCUSSION

The decline in total phosphorus with sediment depth is noteworthy and may be related to recent changes in sedimentation. In 1791, the Tarn was dammed, raising the level of water by about a metre. This has led to erosion of the Tarn Moss peat much of which has ended up in the sediments. Dating by carbonaceous particle analysis indicates that approximately 18 cm of sediment has deposited over the past 150 years (Neil Rose, personal comm.).

Thus the recent increase in phosphorus may correspond to the dam-raising event and thus increased erosion around the Tarn margin. However, the total phosphorus profile suggests that levels had been increasing prior to this. Below 60 cm depth, the Tarn marls contain about 500 ppm total phosphorus similar to the levels reported in the deepest marls of Barton Broad, Norfolk (George, 1996). These marls are thought to have formed during a period when the application of fertiliser and sewage input into Broadland was minimal and represent a lake water ecosystem experiencing little human impact.

The fractionation studies of the recent sediments show considerable variation across the Tarn basin. All of the marl samples contain a substantial fraction of dithionite-extractable phosphorus. The Tarn waters are not depleted of oxygen en masse, but during the productive summer months oxygen levels decline close to the sediments and phosphorus-release almost certainly occurs at this time. In the Bosherton marl ponds, Dyfed, a correlation was found between total phosphorus and total iron in the sediments suggesting a significant fraction of phosphorus was dithionite-extractable (Hinton & Rees, 1989). Phosphorus-release from sediments was enhanced by bioturbation and gas release and the same process probably occurs in the Tarn. The Bosherton ponds receive a high loading of sewage-derived phosphorus in contrast to Malham Tarn. Nevertheless, the levels of total phosphorus in the upper layers of the Tarn sediments are comparable to those of Loch Leven, a well studied, shallow eutrophic lake (Farmer *et al.*, 1994). Here a decline in

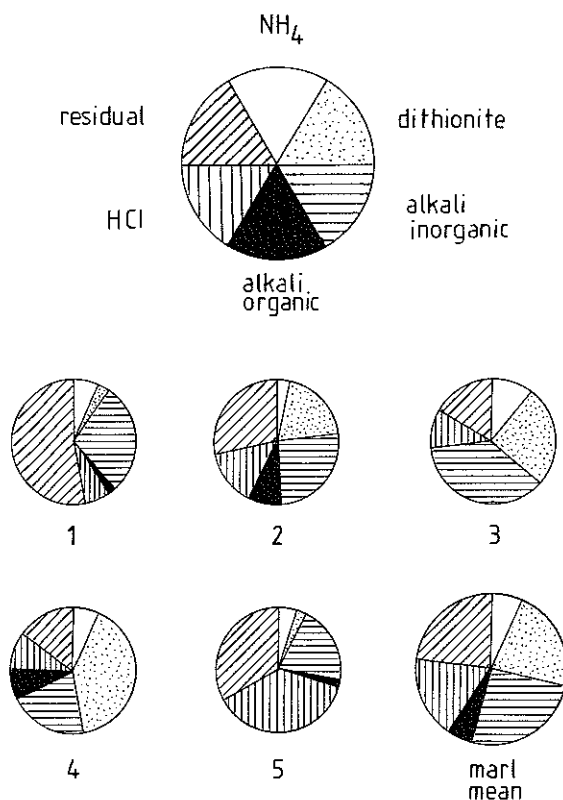


FIG. 3. Pie charts showing the fractionation of phosphorus in the surface sediments of Malham Tarn. Sample 1 is submerged peat, samples 2-5 are marls.

phosphorus with depth has been attributed to recent enrichment via agricultural run-off.

An unexpected result was the high level of alkali-extractable phosphorus bound to oxides since oxides are not a major component of the Tarn sediments. The base-soluble organically-bound phosphorus was low even in the peat sample, and may perhaps indicate leaching of the peat over years of submersion.

The acid-soluble phosphorus is that associated directly with calcium carbonate, the major sediment component. It was the dominant fraction in only the most mineralised sample (no. 5). Therefore, most of the phosphorus appears to be associated with the organic and acid-insoluble fractions (mainly silts and clays) in common with other shallow lake sediments (e.g. Ryding, 1985). Phosphorus may be released from carbonates during summer where there is evidence of carbonate dissolution through the generation of carbon dioxide close to the sediment surface. In addition, as pH is raised, hydroxide may replace phosphorus bound to iron so both a pH fall and pH rise could result in phosphorus loss to the water.

The recent sediment phosphorus-loadings of Malham Tarn suggest some degree of eutrophication which is borne out by increased algal blooms over recent years. However, the processes of nutrient enrichment appears to have begun many years ago, perhaps as early as the 17th Century.

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