

ADVISORY REPORT ON NUTRIENT
LEVELS AND RELATED ECOLOGY
OF MALHAM TARN

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Introduction and scope

This report originated from a meeting held on 26 May 1982 at the Freshwater Biological Association, Windermere, to discuss aspects of reported nutrient levels and their ecological implications for Malham Tarn. The interested parties were: the Nature Conservancy Council, represented by C. Newbold, S. Ward, and S. Priest; the Field Studies Council, represented by E. Jackson; and the Freshwater Biological Association, represented by D.J.J. Kinsman, C.S. Reynolds, J. Hilton, G. Fryer, and J.F. Talling. Discussion centred upon the data given here as Appendices, involving possible evidence of a long-term increase in the concentrations of some nutrients (especially nitrate) of significance for the Tarn's ecology and conservation. During the meeting it was suggested that two developments were desirable, (i) a written critical analysis of the data presented at the meeting, (ii) further comparative tests of some methods of chemical analysis employed in obtaining those data. These matters are treated in the following Sections A and B, written respectively by J.F. Talling and J. Hilton.

A. A critical survey of reported nutrient levels in Malham Tarn, and their limnological significance

Sources of information

Analytical data for the Tarn, and its inflow and outflow streams, are available as follows:

Lund (1961): publication in Field Studies 1 (3), 85-119. Includes analyses for 1949-53 of nitrate-nitrogen ($\text{NO}_3\text{.N}$), soluble reactive phosphate-phosphorus ($\text{PO}_4\text{.P}$), soluble reactive silicon (Si expressed as SiO_2), titration alkalinity, all plotted as seasonal curves based on frequent sampling. Also related information on rainfall, maximum and minimum air temperature, and concentrations of a major planktonic diatom (Asterionella formosa), for 1949-53, 1959-60; lake surface temperature is recorded for 1959-60. Concentrations of all major cations and anions in the Tarn and Tarn Beck for 18-19 June 1958.

Freshwater Biological Association (FBA): besides tabulated records used by Lund (1961), there are similarly tabulated but largely unpublished seasonal analyses for the main inflow from 1951-3, plus later analyses for alkalinity, Ca^{2+} and Mg^{2+} from Dec 1971.

Yorkshire Water Authority (YWA): unpublished records, on computer file, from Jan 1977 - Dec 1981, for the Tarn (south shore); also a few from 1981 for the main inflow. They include $\text{PO}_4\text{.P}$, $\text{NH}_4\text{.N}$, $\text{NO}_3\text{.N}$, $\text{NO}_2\text{.N}$, alkalinity, chloride, pH, and dissolved oxygen.

Central Electricity Generating Board (CEGB): unpublished records, from 20 Nov 1980 and 18 Jan 1981, relating to inflows, the Tarn, and the outflow. They include NO_3 , (? total) P, major cations and anions other than bicarbonate-carbonate alkalinity, and pH.

Pentecost (1981): publication in Field Studies 5 (3), 365-387.

Includes an analysis for the Tarn from 14 May 1973.

The analytical methods used are not given in the paper by Lund (1961) nor in the documents of the YWA. However, the Lund-cited and other FBA data are based on methods described in two FBA publications (Mackereth 1953; Mackereth, Heron & Talling 1978) and most of the recently used YWA methods in YWA (1979). The methods for estimation of nitrate are especially critical. The Lund-FBA analyses were by the phenol-disulphonic acid method, known to yield under-estimates with many fresh waters; the YWA analyses were by the hydrazine-copper method and not the alternative given in YWA (1979) (personal communication); and the CEGB analyses were by the measurement of U.V.-absorption in acid solution containing sulphamate to reduce nitrite interference (Cawse 1967), a method liable to interference by organic matter. No source gives the delay between sampling and analysis, nor the conditions of storage.

Copies of these sources of analytical information are here included as Appendices 1, 2 and 3, 4, 5, and 6 respectively.

Nitrate-nitrogen ($\text{NO}_3\text{.N}$)

Concentrations for the Tarn given by Lund (1961) are based on 4 years (1949-53) of frequent, usually at least monthly, sampling. They show a generally regular seasonal variation between winter-spring maxima and summer-autumn minima. The maxima range between 250-380 $\mu\text{g NO}_3\text{.N l}^{-1}$ during 1949-52 and to only 150 $\mu\text{g l}^{-1}$ in 1953; the minima involve concentrations below 30 $\mu\text{g l}^{-1}$ in all 4 years. The extended periods of low concentration are never broken by sudden episodes of high ($> 100 \mu\text{g l}^{-1}$) concentration, even when rainfall was heavy as in August 1950. A single such episode interrupts the usual vernal decline of concentration in

May 1949.

The unpublished 1951-3 analyses of concentrations in the major inflow (Tarn Beck) can be instructively compared with the simultaneous analyses for the Tarn. Concentrations in winter are usually higher in the inflow but generally not greatly so. Inflow concentrations in summer are sometimes very low ($< 50 \mu\text{g l}^{-1}$) for short periods, but generally are much higher over most of the prolonged summer-autumn periods of low concentrations in the Tarn. During 1951, but not in other years, there is evidence for pulses of nitrate-rich ($> 300 \mu\text{g l}^{-1}$) inflow water in May, July, and October; these have no obvious effect on the then low ($< 60 \mu\text{g l}^{-1}$) concentrations in the Tarn. One may deduce that from spring to autumn there is (i) a strong net consumption of nitrate in the Tarn, as well as (ii) a vernal reduction in nitrate in the drainage from the catchment. Lund (1961) interprets nutrient uptake such as (i) as predominantly due to the growth of aquatic macrophytes in the Tarn, rather than of the generally sparse phytoplankton; for (ii) he suggests vernal uptake of nitrogen by plants in the drainage area as they restart seasonal growth. Losses by bacterial denitrification are possibly also of significance.

All these FBA analyses were done using the phenol-disulphonic acid (PDS) method, which is prone to an interference and known to under-estimate the concentrations of nitrate in many natural waters. Detailed tests of this analytical problem are given in Section B. This shows that a correction is probably complex and non-linear. The best approximation offered would increase most recorded concentrations ($> 50 \mu\text{g l}^{-1}$) by approx. 40-60%, and lower concentrations by a greater percentage but small absolute amount.

The available analyses of Tarn water by the YWA (hydrazine-copper method) also involve 4 years, with roughly monthly sampling. No useful comparison can be made with the main inflow for which only three analyses

are recorded. In broad outline the concentrations of nitrate-nitrogen in the Tarn vary between generally high concentrations (maxima $> 500 \mu\text{g l}^{-1}$, usually $> 1000 \mu\text{g l}^{-1}$) in winter and low concentrations (minima $< 50 \mu\text{g l}^{-1}$) in summer. The broad seasonal trend is similar to that of the earlier FBA analyses, but differ in that (i) the winter maximum concentrations are much higher, by a factor of 3 or more, and (ii) the low summer concentrations are often broken by isolated instances of higher concentration. The first difference is much greater than the probable analytical under-estimation of the early FBA analyses. If possible changes during sample storage (unlikely, in my opinion, to be a major factor in winter) can be neglected, the difference is probably real and reflects a larger winter input of nitrate to the Tarn in 1977-81 than in 1949-53. Such a persistent difference is unlikely to be related to variable amounts of precipitation. The reality of the difference is also supported by the analysis of Tarn water by the FBA in September 1982 (see Section B), when the PDS as well as the hydrazine-copper method yielded higher estimates than were obtained in the same month during 1949-53. The second difference (ii) also suggests a change, to a larger and more discontinuous input of nitrate during summer in later years. Nevertheless the lowest concentrations are of the same order in both periods, and from the inflow-Tarn comparison of the FBA are likely to be strongly influenced by nitrate consumption in the Tarn as well as by uptake in the catchment.

The two sets of CEGB analyses (U.V.-absorption method: Cawse 1967) were based on winter sampling, on 20 Nov 1980 and 18 Jan 1981. They include both main inflow (Nov 2270, Jan 510 $\mu\text{g NO}_3\text{-N l}^{-1}$) and Tarn (Nov 1970, Jan 650 $\mu\text{g l}^{-1}$). The Tarn values lie within the range of winter concentrations in YWA analyses, discussed above, but the November CEGB value of 1970 $\mu\text{g l}^{-1}$ is much higher than YWA values around that period (e.g. 130 $\mu\text{g l}^{-1}$ on 2 Nov 1981, 280 $\mu\text{g l}^{-1}$ on 1 Dec 1981). Thus the high November value is

questionable. The method used is prone to interference by coloured organic material, which would lead to overestimation of nitrate.

A single analysis of Tarn water is reported by Pentecost (1981) (Appendix 6) from 14 May 1973; the cadmium-copper reduction method yielded the very low value of $0.07 \mu\text{M}$ or $1 \mu\text{g NO}_3\text{.N l}^{-1}$.

Summarising, and with allowance for known analytical error, there is evidence for marked increase in nitrate input to the Tarn between 1949-53 and 1977-81. However the high CEEB estimates for Nov 1981, which originally drew attention to the problem, are open to doubt. All sufficiently extensive data (of FBA and YWA) indicate a strong seasonal cycle between high winter and low summer concentrations in the Tarn. The spring-summer decrease is due partly to decrease of nitrate in land run-off, partly to uptake (macrophytes, possibly bacteria) in the Tarn.

Phosphate-phosphorus ($\text{PO}_4\text{.P}$)

Seasonal data for the Tarn are given by Lund (1961) and YWA for 1949-53 and 1977-81 respectively. Unpublished FBA data add some seasonal information for the main inflow during the first period. There is no reason to suspect systematic bias of the analytical methods used; the chief analytical problem is one of low sensitivity in relation to the small concentrations encountered.

More than half the 1949-53 concentrations for Tarn and inflow lie on or below the limit of detection, then assessed as $1 \mu\text{g PO}_4\text{.P l}^{-1}$. The highest concentration recorded was only $3 \mu\text{g l}^{-1}$, and values above $2 \mu\text{g l}^{-1}$ were uncommon. Seasonal trends cannot be discerned, and the inflow concentrations are generally not higher than those of the Tarn.

The 1977-81 YWA Tarn analyses have a much higher limit of detection, at various times being 10 or $20 \mu\text{g PO}_4\text{.P l}^{-1}$. If no change had occurred since 1953, all results would be expected to be below the limit of

detection. Most are indeed so recorded, but about one third range from 20 to $60 \mu\text{g l}^{-1}$, with no evident seasonal regularity. In view of the high limit of detection, and the possibility that higher values might arise from only slight contamination, the few higher values are uncertain evidence for a long-term increase since 1953.

In such water where the precipitation of CaCO_3 occurs annually on a considerable scale (see later section on alkalinity), it is likely that a concomitant removal of phosphate from solution occurs. More is likely to be removed by plant growth, especially macrophytes, in the Tarn. Thus considerable changes in P income might be masked by loss processes. Analyses of total phosphorus in suspension or solution might have aided interpretation, but only a single low value ($3 \mu\text{g P l}^{-1}$) is available from Pentecost (1981, Table 3) (Appendix 6) for 14 May 1973. There appear to be no adequate recent analyses of $\text{PO}_4\text{-P}$ in inflows. One would expect a considerable increase there since 1953 due to the use of modern detergents rich in phosphate at the Field Centre and farms, to increased agricultural activity reported beside at least one tributary stream, and possibly to changes in grazing practice.

Soluble reactive silicon (Si), reported as silica, SiO_2 .

The 1949-53 analyses of Tarn water given by Lund (1961) show higher winter concentrations generally of $1\text{-}2 \text{ mg SiO}_2 \text{ l}^{-1}$ ended by a spring decrease to values below 0.5 mg l^{-1} about May. The subsequent recovery in summer and autumn may be irregular. Strong declines, as in spring, are related to biological uptake by growing populations of diatoms, for which Lund gave quantitative data on the seasonal abundance of one principal planktonic species (*Asterionella formosa*). He showed, however, that uptake by the rich bottom-living diatom communities is probably the greatest source of loss. Concentrations in the main inflow were generally higher than those

in the Tarn, as shown by unpublished FBA records (Appendix 2). The analytical method used (reaction with acid molybdate, without reduction) is now known from FBA experience to be unreliable for the lowest concentrations below $0.5 \text{ mg SiO}_2 \text{ l}^{-1}$, which can be overestimated. This does not seriously affect the majority of analyses, at higher concentrations.

The 1977-81 records of the YWA include a few analyses for the Tarn and its main inflow. They are given only to 1 figure, and the range of $1-3 \text{ mg SiO}_2 \text{ l}^{-1}$ is broadly consistent with the earlier analyses.

Alkalinity (largely bicarbonate) and related variables

Lund (1961 Fig. 6) showed that the alkalinity of the main inflow was generally much higher than that of the Tarn water, and that both had large seasonal variations although in opposite directions. Thus there were summer minima ($< 100 \text{ mg CaCO}_3$ or 2 meq l^{-1}) in the Tarn but summer-autumn maxima ($> 200 \text{ mg CaCO}_3$ or 4 meq l^{-1}) in the inflow. He (in his Appendix IV) interpreted these changes as due to precipitation or re-solution of CaCO_3 governed by changes of CO_2 concentration, the last induced by plant photosynthesis, temperature effects on gaseous solubility, air-equilibration, and CO_2 supply to soil and underground drainage. These factors (especially air-equilibration) were later studied by Pentecost (1981), who suggested that precipitation of calcite by the stonewort Chara globularis might account for the variability of hardness and pH across transects of the Tarn. The seasonal alkalinity changes imply similar changes (as equivalents) in Ca^{2+} , and the absolute magnitude of both is larger than those of any other chemical constituent.

The 1977-81 analyses of the YWA also establish a large seasonal variation in the alkalinity of Tarn water. The absolute magnitude and the seasonal pattern of alkalinity are similar to those given by Lund, but the summer minima are often lower, all below 80 mg CaCO_3 or 1.6 meq l^{-1} . The

last feature may indicate enhanced precipitation of CaCO_3 by increased plant growth in the Tarn. Pitty (1971, Fig. 2) also found a summer fall of alkalinity, for 1964-65, but only to a value of $111 \text{ mg CaCO}_3 \text{ l}^{-1}$ or 2.22 meq l^{-1} . He demonstrated a strong inverse correlation between alkalinity and average air temperature during the 5 weeks before sampling, and interpreted the summer decrease as due mainly to the uptake of CO_2 by aquatic plants.

Alkalinity is here cross-correlated with several other chemical or physico-chemical variables. In the pH range involved, it is generally almost synonymous with bicarbonate (HCO_3^-) concentration, and very similar to Ca^{2+} concentration, when all are expressed in meq l^{-1} (note $50 \text{ mg CaCO}_3 \text{ l}^{-1} \equiv 1 \text{ meq l}^{-1}$). As HCO_3^- is by far the dominant anion, alkalinity is closely correlated with electrical conductivity (approximately, 1 meq l^{-1} alkalinity $\approx 100 \text{ } \mu\text{S cm}^{-1}$ (25°C)), itself an index of total ionic content. Recently seasonal measurements of conductivity and alkalinity have been obtained (Woof & Jackson, in prep.). If the waters of the Tarn were in gaseous equilibrium with the atmosphere, pH values of 8.0-8.5 could be anticipated from the bicarbonate alkalinity. Such values are common in the YWA records, but there are some higher values (e.g. 8.8-9.2 in May-July 1978) which suggest CO_2 -depletion by photosynthesis.

Major cations

Analyses for the four ions involved - Ca^{2+} , Mg^{2+} , Na^+ , K^+ - are given by Lund (1961, Table 1) for the Tarn and its main inflow during 18-19 June 1958. Later analyses (FBA 1971 unpubl., Appendix 3; Pentecost 1981, Appendix 6; Woof & Jackson in prep.) confirm the strong predominance of Ca^{2+} and the low concentration ($\sim 20 \text{ } \mu\text{eq l}^{-1}$) and relative proportion ($\sim 0.4\%$) of K^+ . Marked seasonal cycles of Ca^{2+} in Tarn and inflow water can be deduced from the alkalinity cycles, although not documented by direct

analyses before the recent study of Woof & Jackson (in prep.).

In December 1971 analyses of Ca^{2+} and Mg^{2+} concentrations, and their ratios, were made by the FBA for various localities around the Tarn (Appendix 3). An analysis from 14 May 1973, which includes all major cations and anions, is given by Pentecost (1981, Table 3) - see Appendix 6.

Tarn hydrology and chemical dynamics

For interpretation of chemical changes in the Tarn it is desirable to have estimates of the rate of water replacement. A detailed hydrological study of the Tarn does not seem to exist, but the following physical quantities (estimates from information of Lund (1961, *) or from Mr E. Jackson) are important:

* area	= 0.62 km ²	volume	= 1.5 × 10 ⁶ m ³
mean depth	= 2.5 m	catchment area	= 6.3 km ²
* max. depth	= 4.4 m	* mean annual rainfall	= 1500 mm

From these figures, and assuming a rough factor for land run-off of 0.8 (possibly a large overestimate for fissured limestone country), the mean replacement time (i.e. lake volume/mean inflow rate) is roughly estimated as 72 days. In months of heavy rain this will be reduced; from the data in Lund (1961) a monthly rainfall of 240 mm is not uncommon, which would yield an estimated replacement time of 37 days. In a well-mixed water-body the water-mass would only be partly replaced by inflow water (an exponential process) in these "replacement times". During them one would then expect an initial concentration difference between mean inflow and Tarn water to be reduced to 37%, provided that the inflow concentration is maintained and the quantity involved is conservative (i.e. not subject to relatively rapid secondary changes, such as are possible from biological uptake of nitrate or exchanges of CO_2 affecting alkalinity). For winter conditions, when lacustrine generation and biological uptake of nitrate are minimal and

differences between nitrate concentrations in Tarn and inflow are reduced, the calculated replacement time is probably longer than would be needed to produce such large and rapid changes of nitrate concentration in the Tarn as that implied by the CEGB analyses for Nov 1980 - Jan 1981.

Abundance and composition of aquatic vegetation in relation to chemical variables

Vegetation in the Tarn consists of (i) submerged macrophytes, (ii) bottom-living (stone-attached or on sediments) algae, and (iii) phytoplankton. Past descriptions include: for (i), Sledge (1936) and Sinker (1960); for (ii), Round (1953), Lund (1961), and Pentecost (1975, 1978); for (iii), Lund (1961).

There do not appear to be estimates of total biomass density for any of these three components. Lund (1961) believed that the non-planktonic forms were greatly in excess of the phytoplankton, and so would dominate the uptake of such nutrients as N and P. Even silicon, required by diatoms and seasonally subject to near-complete depletion, seems to be mainly consumed by benthic diatoms; judging from 1949-53 data, quantities incorporated in the planktonic crops are not large (Lund 1961). Nevertheless, there is evidence that the Si depletions attributable to benthic growth can limit the growth of a major planktonic diatom, Asterionella formosa.

According to Lund (1961 p. 97), 'the plankton of the Tarn is qualitatively that of a somewhat eutrophic body of water but quantitatively it is usually rather sparse, though considerable crops arise occasionally'. The plankton diatom Stephanodiscus hantzschii is generally accepted to be an indicator of eutrophy, and was noted in some quantities by Lund during 1950-3 but not in the years immediately following. A large crop was recorded in 1952.

The high base status (Ca^{2+} , alkalinity) of the Tarn may possibly

unduly influence such interpretations of eutrophy from indicator species, as elsewhere such status is generally indirectly correlated with nutrient-rich environments (as in highland/lowland comparisons). Qualitatively the high concentrations of the two major ions Ca^{2+} and HCO_3^- is a basis for abundance of typically CaCO_3 -encrusted species, such as species of Chara (Stoneworts) abundant in the Tarn and the attached blue-green algae Schizothrix calcicola, Rivularia haematites and Microcoleus vaginatus studied at Malham by Pentecost (1975, 1978, 1981). Pentecost showed that the precipitation of CaCO_3 by felts of the blue-green algae was not primarily due to the removal of CO_2 by photosynthesis.

Summary and conclusions

1. A review is given of the chemical composition of waters from Malham Tarn and its main inflow, with particular reference to plant nutrients and to possible long-term changes. Four main sources of analyses are described. Two from the FBA refer mainly to the period 1949-53, one from the YWA to 1977-81 and one from the CEGB to 1980-1. Special attention is given to seasonal changes and to the comparison (largely from unpublished FBA data) of Tarn water with its main inflow.
2. Concentrations of nitrate in the Tarn vary seasonally between winter maxima and summer minima. A vernal decline is due partly to changes in drainage and inflow, partly to uptake in the Tarn. Compared to the 1949-53 FBA values, the 1977-81 YWA records show considerably higher concentrations in winter and a greater interruption of low summer values by short phases of higher concentration. These differences are greater than can be attributable to an underestimate (probably usually 40-60%) in the earlier FBA method of analysis. The few CEGB analyses from 1980-1 include a high Tarn concentration in November that is open

to doubt.

3. Most estimates of soluble reactive phosphate in Tarn and inflow water are below the limits of detection. The few higher values in 1949-53 did not exceed $3 \mu\text{g PO}_4\text{-P l}^{-1}$. Much higher values present in the YWA records for 1977-81 require confirmation in view of the relatively insensitive method then used (limit of detection about 10 or 20 $\mu\text{g l}^{-1}$) and the possibility of contamination.
4. Soluble reactive silicon (here expressed as silica) varies seasonally in the Tarn, and to a small extent in the main inflow, probably chiefly from uptake by benthic diatoms. Planktonic diatom production is probably a minor agent of silicon consumption, although the growth of at least one species can be limited by its depletion. There is no evidence of long-term changes from the limited 1977-81 data.
5. The alkalinity (largely bicarbonate) of the Tarn water shows large seasonal variation in both older and more recent analyses, with winter maxima and summer minima. The more recent minima tend to be lower. Another large variation, but of opposite direction, occurs in the main inflow where values are always higher. These changes must be regulated by varying CO_2 content. There are implications, some supported by further analyses, for several correlated quantities including Ca^{2+} concentration, electrical conductivity, and pH. Some information also exists for other major cations (Mg^{2+} , Na^+ , K^+).
6. Rough estimates of water retention time in the Tarn are derived from rainfall, drainage area, and morphometry. Their implications for chemical changes induced by inflow are noted.
7. Scanty information on the relation between water composition and some quantitative and qualitative features of aquatic plant communities is discussed.

B. Comparison of analytical methods for nitrate

Phenol-disulphonic acid method vs hydrazine-copper method

Most of the nitrate data available for Malham Tarn were obtained by one of two analytical methods - the phenol-disulphonic acid method or a reduction to nitrite by hydrazine with a copper catalyst followed by determination of the nitrite with sulphanilamide/naphthyl ethylene-diamine dihydrochloride. The former method, hereafter called the PDS method, was used by Lund, while the latter, hereafter called the hydrazine-copper method, was used by the Yorkshire Water Authority. A U.V. absorption method was used in a few analyses (2 dates only) by the CEGB.

The PDS method is used routinely at the FBA River Laboratory while the hydrazine-copper method is used here at the Windermere Laboratory. Previous, unpublished work (Heron), had suggested that, for Windermere water, either a constant bias of the form hydrazine-copper analysis = PDS analysis + constant or a percentage error (Sutcliffe et al. 1982) is present depending on the data set used. In order to investigate the possibility that differences in the analytical results taken at different times may only reflect changes in analytical methods, the following series of tests were carried out:

- a) A single sample from Malham Tarn was analysed in replicate by both methods.
- b) Natural water samples were left in order to allow nitrate to be consumed. Known amounts of nitrate were then added and analysis performed.
- c) Water samples were sampled with time and analysed for nitrate.

A sample was taken from Malham Tarn on 22 April 1982 by Mr C. Woof. On arrival at the Windermere Laboratory 6 replicates were analysed by the hydrazine-copper method while 6 further replicates were evaporated to dryness before being transported to the River Laboratory for analysis by the

PDS method. The results, given in Table 1, show that the PDS method gave a result which is $207 \mu\text{g l}^{-1}$ (or 36%) less than that of the hydrazine-copper method.

In order to determine which method actually gave the correct results, and also to see if the bias was a simple subtraction or a percentage reduction, a further set of analyses were carried out. A 20-l sample of Malham Tarn water was collected on 30 June 1982 by Mr C. Woof and stored for a month to allow the nitrate concentration to be reduced to zero. On 6 August (when measurement of nitrate gave a concentration below the limit of detection) several litres of this sample were filtered through a GFC filter and the resulting filtrate used to prepare solutions of known nitrate concentration. A fresh sample of Windermere water was collected and, since the nitrate concentration was not detectable in the lake, filtered within two days and a further set of nitrate samples of known concentration made up. A series of standards was also made up in deionised water to act as a control. These samples were randomised and nitrate was measured by the hydrazine-copper method. At the same time, duplicate samples (100 ml each) were evaporated down prior to transport to the River Laboratory for analysis by the PDS method. The results are given as mean values in Table 2 and plotted (analytical estimate versus known concentration) in Figures 1a, b, c. These Figures show that, when allowance is made for the difference in the blanks, the calibration lines in deionised water (Fig. 1a) are the same with a slope of 1. The Windermere water (Fig. 1b) produces a bias, as previous results suggested it might. However, although a straight line can be drawn through the points (excluding the blank) a more likely representation is a curve. The Malham Tarn water (Fig. 1c) shows an unexpected result. Although there are differences in the slopes and intercepts, for the two methods, they are minor when compared with the differences observed on the Windermere sample.

The lack of a large bias is unusual and may have several reasons (see later). An important point from all these results, however, is that the hydrazine-copper method is likely to give the correct result whereas the PDS method may, or may not, give lower results.

The lack of bias with Malham water samples in this second set of analyses is inconsistent with the replicates taken earlier. There are at least two possible reasons for this:

a) The interferant causing bias in the PDS method may vary in concentration throughout the year. This would only be answered by a long-term comparison of methods.

b) The concentration of interferant changed during the storage period and was reduced along with the original nitrate. In order to test this hypothesis a further series of analyses were carried out.

A sample of Malham Tarn water was taken by the staff of the Field Study Centre on 14 September 1982 and delivered to the FBA Windermere Laboratory on the same day. Immediately on receipt of the sample, several litres were filtered and sufficient sodium nitrate added to make the concentration approximately 300 $\mu\text{g NO}_3\text{.N}$. The preparation was repeated with a sample of Windermere water. At irregular periods over the next 14 days sub-samples were taken and immediately analysed by the hydrazine-copper method, while duplicate samples were evaporated prior to transport to the River Laboratory for analysis by the PDS method. The mean results are recorded in Table 3 and in Figure 2a, b.

The immediate conclusion is that a bias in the PDS method has appeared again in the Malham results. The results are less conclusive as regards the original reason for carrying out the experiment, namely explanation of the lack of bias in experiment 2. Although a slight lowering of the nitrate concentration with time is observed for the Malham sample it is very small and is apparent in both samples rather than a convergence of the PDS value

towards the hydrazine-copper value as might be expected. One reason may be that, in order to preserve the nitrate, the samples were filtered prior to storage. This will have reduced algal and bacterial action and may have stopped the removal of interferants from the samples. The bias between samples has been presented in Table 3. It has also been expressed as a percentage of the hydrazine-copper result.

There is no simple consistent measure of the magnitude of the bias from all the data. Figure 1b suggests that the calibration line is curved so that neither a single addition to the PDS value nor the addition of a percentage will be a generally adequate correction. This can be appreciated more clearly in Figures 3a and b where the difference between the two readings (Fig. 3a) or the difference as a percentage of the actual or hydrazine-copper given concentration (Fig. 3b) is plotted against the actual or hydrazine-copper given concentration. The plot of absolute difference between the two methods does approximate a straight line ($r = 0.85$). Within the large scatter the line could pass through zero but this is unlikely since the percentage plot (Fig. 3b) is parabolic. The intercept is of the same order as the limit of detection of the hydrazine-copper method which was used as a test that all the nitrate had disappeared in the calibration experiments. Hence it is only important at the lowest concentrations. It could, however, be affected by the Malham and Windermere blanks containing non-detectable amounts of nitrate. If the worst case is assumed, i.e. that $14 \mu\text{g l}^{-1} \text{NO}_3\text{-N}$ (the limit of detection) is present in the blank, then the percentage plot (Figure 3b) is still non-linear and the intercept in the difference plot (Figure 3a) is slightly altered. The regression line can be used as a best estimate of the bias from this work:

$$\text{bias} = 0.273 \text{ Actual} + 7.69$$

$$\text{or, since Actual} = \text{PDS} + \text{bias}$$

$$\text{Actual} = 1.38 \text{ PDS} + 10.6$$

Conclusions

- i) There is a difference between nitrate values measured on natural water samples by the hydrazine-copper method and the PDS method.
- ii) It is likely that the hydrazine-copper results are near-correct, and that the PDS method has a negative bias.
- iii) The extent of bias may vary throughout the year but this has not been confirmed.
- iv) The bias apparently produces a curved calibration line, so that neither addition of a single extra amount of nitrate to the PDS value nor addition of a fixed percentage will be a generally adequate correction.
- v) The data presented here suggest that the best approximate correction in the circumstances is to use the formula : corrected value = 1.38 PDS value + 11 $\mu\text{g NO}_3\text{-N}$.

U.V. absorption method (Cawse 1967)

The analysis depends on the measurement of the absorption peak at 210 nm due to nitrate. Nitrite interference is reduced by the addition of sulphonic acid. Colloidal organic interferences can be removed by addition of aluminium paste. Dissolved organics are not removed. Hence the CEGB results will tend to be higher than results from a more interference-free method such as hydrazine-copper. This bias will be arbitrary depending on the concentration and composition of organic matter in solution.

Table 1. Results of analysis (in $\mu\text{g NO}_3\text{-N l}^{-1}$) of a single sample from Malham Tarn, 21 April 1982.

		n	\bar{x}	s
PDS	340, 340, 340, 380, 400, 400	6	367	30
hydrazine-Cu	560, 566, 572, 580, 582, 582	6	574	9

Table 2. Mean values (from duplicates) of $\text{NO}_3\text{-N}$ concentrations (in $\mu\text{g l}^{-1}$) measured on known additions to three different basal media using the PDS and hydrazine-copper methods.

	Blank	50	100	200	300	400
<u>Deionised</u>						
PDS	9	66	111	207	309	419
hydrazine-Cu	1	55	100	199	301	402
<u>Malham Tarn</u>						
PDS	-	76	130	213	297	372
hydrazine-Cu	13	60	106	198	294	379
<u>Windermere</u>						
PDS	13	21	60	121	223	320
hydrazine-Cu	8	62	104	209	306	401

Table 3. Analyses of two samples ($\mu\text{g NO}_3\text{-N l}^{-1}$) by different analytical methods after various periods of time.

day,	Malham Tarn				Windermere			
	PDS	hydrazine-	diff.	% diff.	PDS	hydrazine-	diff.	% diff.
Sept 1982	Cu (b)	(a)	(100 a/b)	Cu (d)	(c)	(100 c/d)		
14	213	291	78	26.8	201	294	93	31.6
15	223	298	75	25.1	200	305	105	34.4
16	216	293	77	26.3	220	302	82	27.2
17	207	295	88	29.8	212	303	91	30.0
21	201	293	92	31.3	212	303	91	30.0
22	207	280	73	26.1	204	298	94	31.5
28	198	260	62	23.8	216	289	73	25.2
Mean			77.9	27.0			89.9	30.0
Standard devn.			9.89	2.63			10.0	3.03
s.d. as % of mean			12.7	9.70			11.2	10.1

Fig 1. Plots of the concentration of nitrate as measured on water samples to which known amounts of nitrate have been added to form a solution of known concentration.

1a) Deionised water.

$PDS = 1.010 \text{ Actual} + 10.1 \quad r = 0.9996$ - - - -

$\text{hydrazine-Cu} = 0.998 \text{ Actual} + 1.7 \quad r = 0.9999$ ————

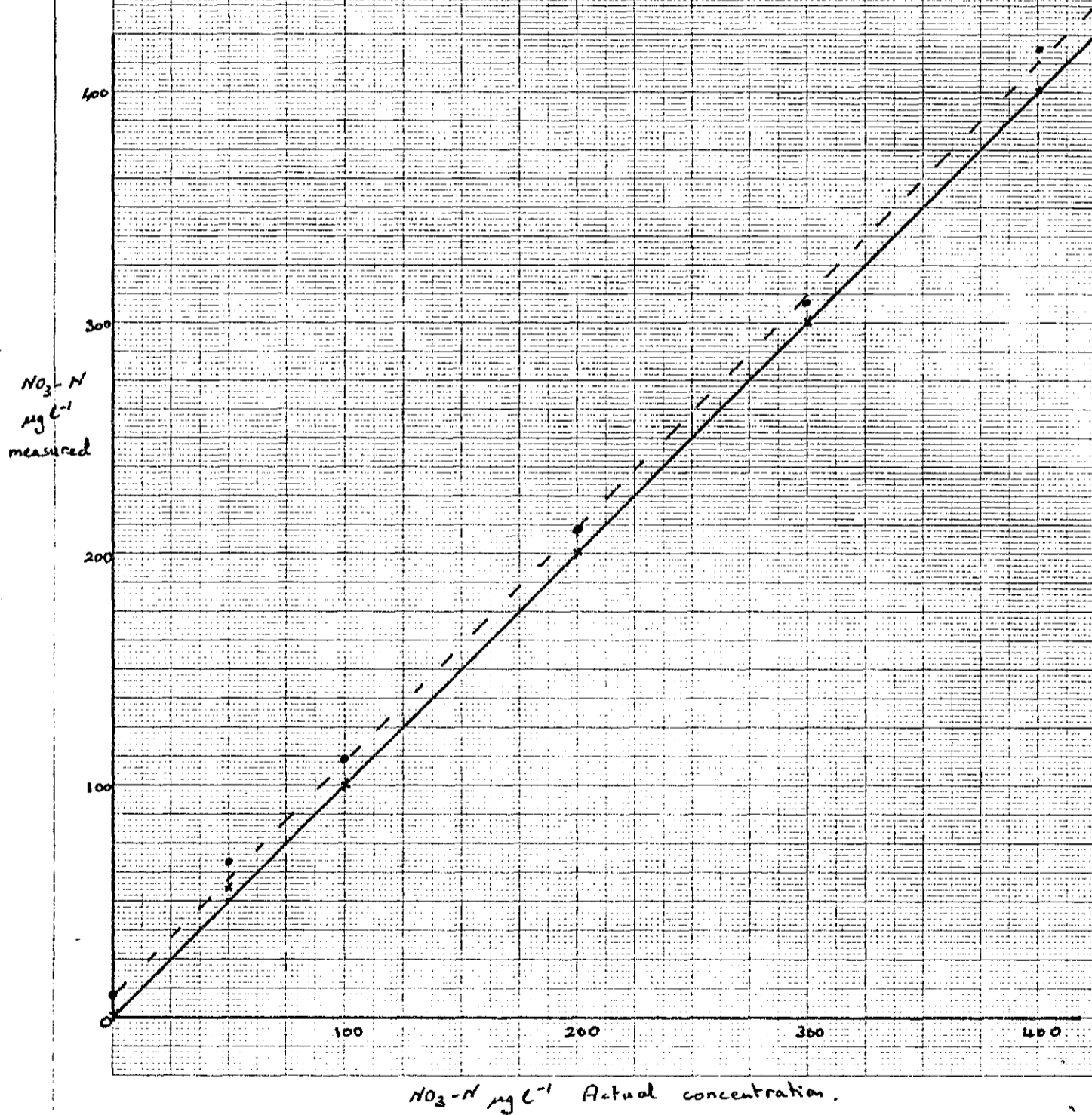


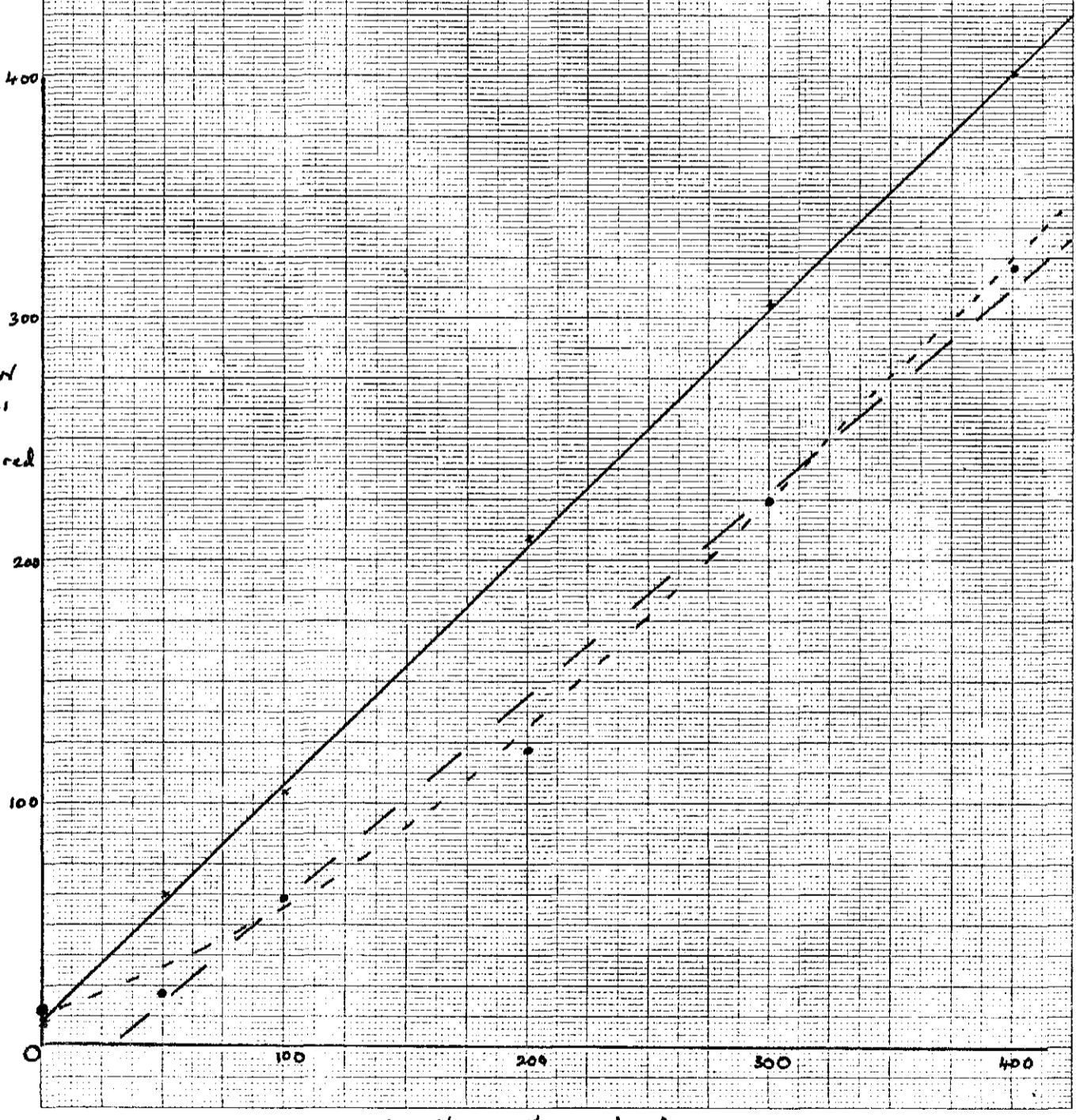
Fig 1b. Windermere water.

$PDS = 0.850 \text{ Actual} - 29.5 \quad r = 0.9953 \text{ (excluding blank)}$

$\text{hydrazine-Cu} = 0.983 \text{ Actual} + 9.6 \quad r = 0.9998$

hand-drawn curve to fit PDS data

$\text{NO}_3\text{-N}$
 $\mu\text{g l}^{-1}$
measured



$\text{NO}_3\text{-N}$ $\mu\text{g l}^{-1}$ actual.

Fig 1c Malham Tarn water.

PDS = $0.839 \text{ Actual} + 41.4$ $r = 0.9989$ - - - - -

hydrazine-Cu = $0.920 \text{ Actual} + 14.0$ $r = 0.9999$ _____

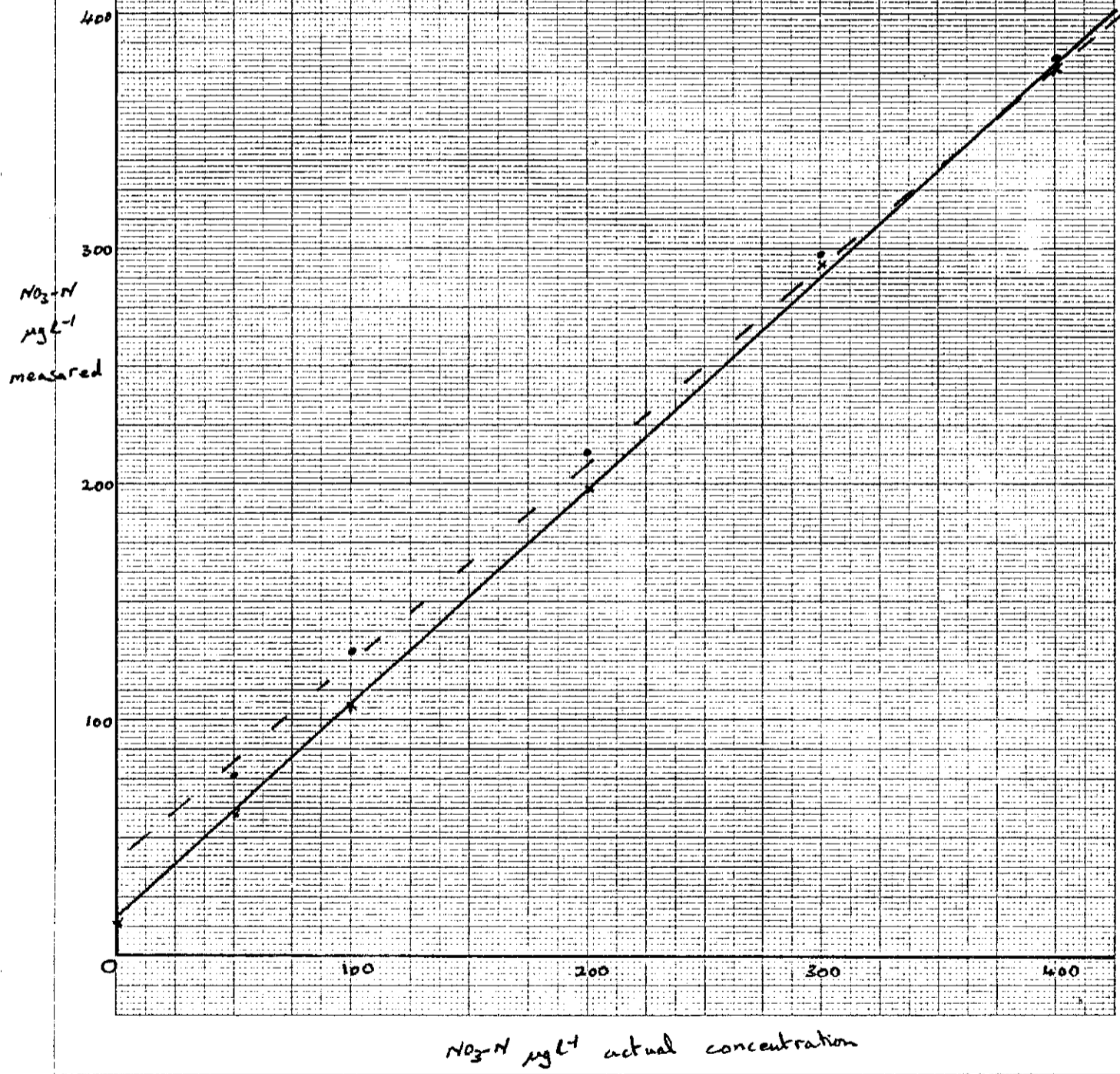


Fig 2 . The change in measured nitrate concentration with time as measured by the two analytical methods.

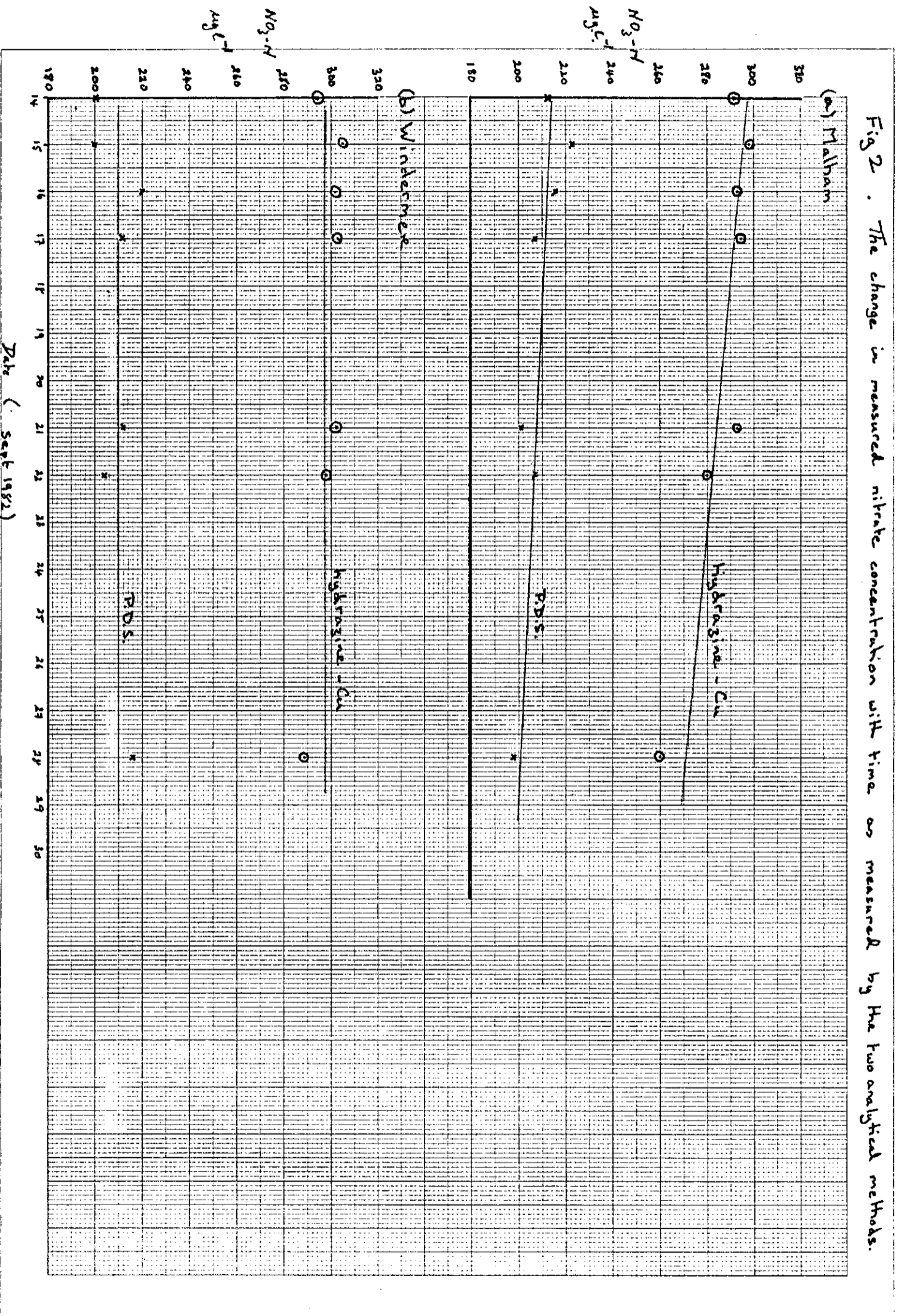


Fig. 3a. The difference between the results from the two analytical methods plotted as a function of the actual concentration.

difference = 0.233 DVA conc. + 3.3 $r = 0.85$

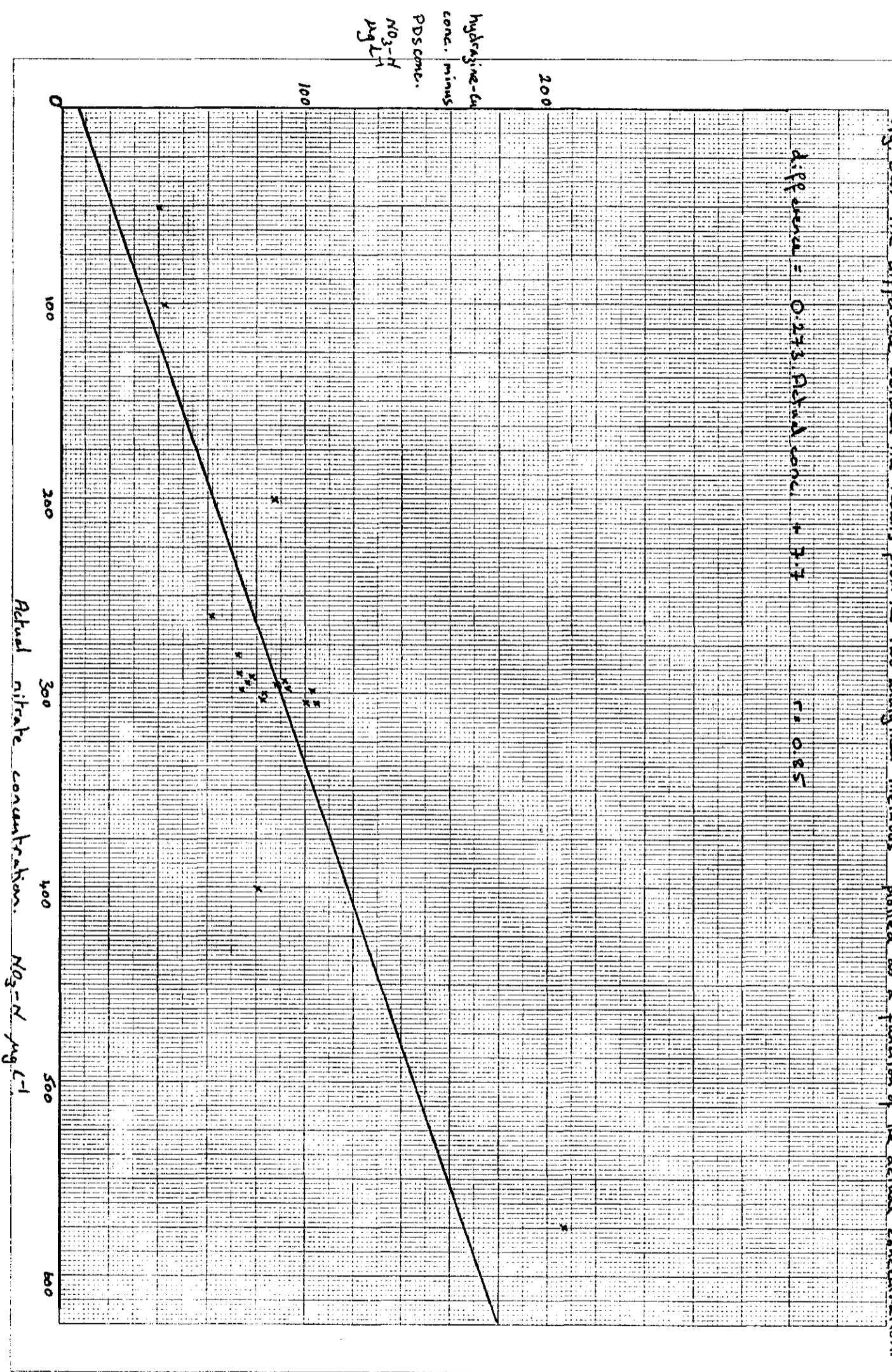
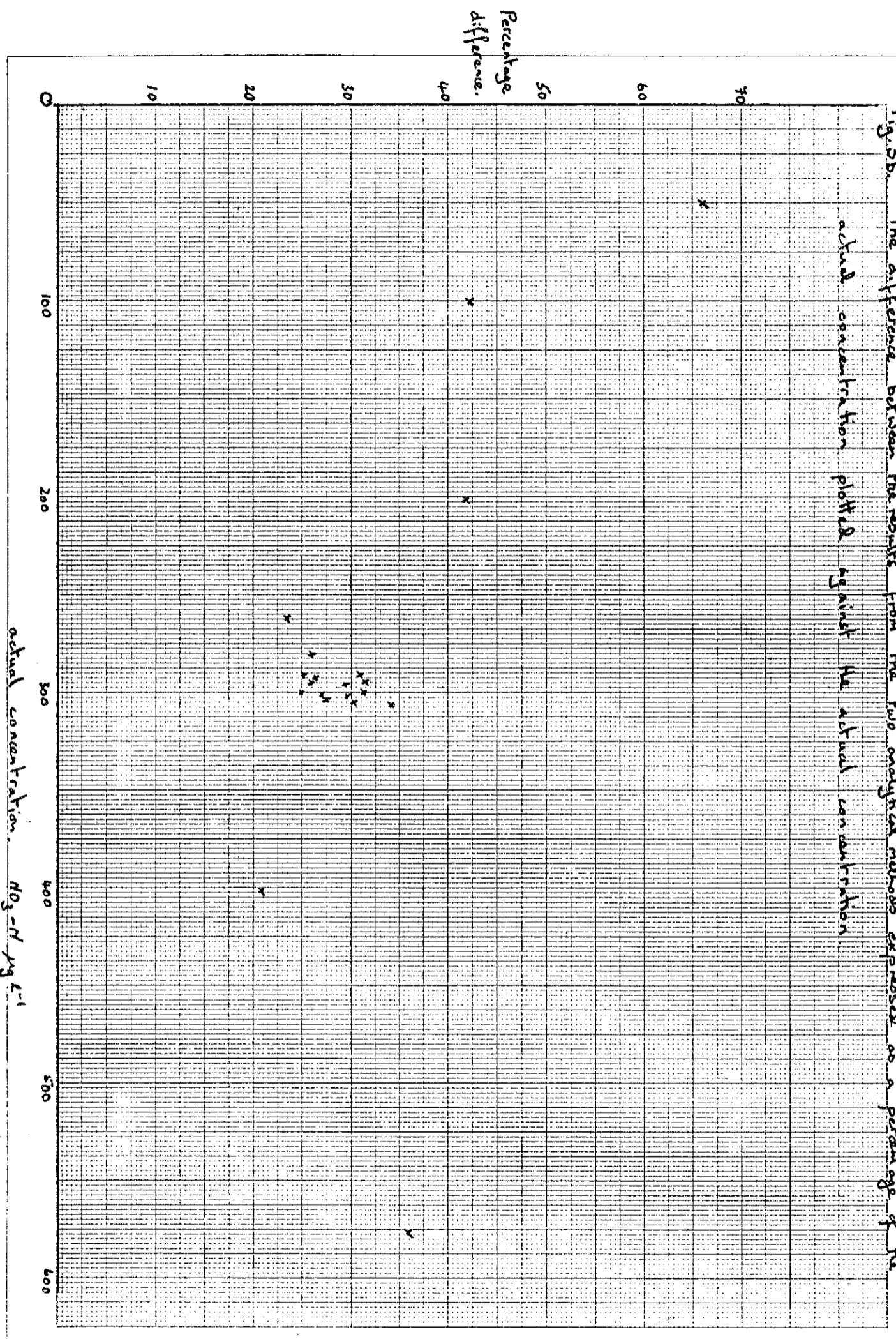


Fig. 3b. The difference between the results from the two analytical methods expressed as a percentage of the actual concentration plotted against the actual concentration.



Acknowledgements

We are indebted to staff of the YWA and CEGB for making their unpublished data available; to past and present staff of the Malham Tarn Field Centre, especially Mr E. Jackson, and to Mr C. Woof (FBA), for collection of many samples and for additional information; to the late Mr F.J.H. Mackereth and Mr J. Heron for early unpublished analyses; to E. Rigg and H. Casey (FBA) for recent analyses in the experimental work; and to Mrs J.C. Rhodes for preparing the typescript and copies of data.

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Appendices

1. Publication by Lund (1961).
2. FBA analytical data for Malham Tarn and its main inflow, Tarn Beck, 1951-53.
3. FBA analytical data on concentrations of Ca^{2+} , Mg^{2+} , and their ratio, in waters around the Tarn in December 1971.
4. YWA analytical data for the Tarn at its outflow, and the main inflow, 1977-81.
5. CEGB analytical data for the Tarn and nearby streams, including the main inflow, from sampling on (a) 20 Nov 1980 (b) 18 Jan 1981.
6. Pentecost (1981): Tables of chemical analyses for the Tarn and nearby streams.

MALHAM TARN. 1951. All results in milligrams/litre.

	<u>Inflow sample.</u>				<u>Tarn sample.</u>			
	<u>SiO₂</u>	<u>NO₃N.</u>	<u>PO₄P.</u>	<u>Alkalinity as CaCO₃</u>	<u>SiO₂</u>	<u>NO₃N.</u>	<u>PO₄P.</u>	<u>Alkalinity as CaCO₃</u>
January								
February								
March								
April								
24	0.90	.09	.001	166.3	0.50	.13	.001	115.5
May								
8	1.10	.02	.001-	138.7	0.25	.07	.001-	116.0
19	0.80	.40	.001-	172	0.30	.05	.001-	116
June								
8	0.50	.14	.001	171	0.30	.02	.001-	124
26	0.57	.25	.001-	182	0.35	.01	.001-	111
July								
9	1.00	.22	.001-	132	0.43	.02	.001-	102
23	1.30	.36	.001-	191	0.90	.03	.001-	92
August								
6	1.00	.18	.001-	185	0.72	.03	.001-	85
17	1.70	.04	.001	163	0.90	.03	.001-	80
September								
13	1.70	.03	.001-	218	0.90	.02	.001-	88
27	1.70	.02	.001-	216	1.10	.02	.001-	93
October								
10	1.70	.38	.001-	218	0.88	.05	.001-	98
29	1.40	.27	.001-	209	0.75	.02	.001-	97
November								
5	1.50	.05	.001-	165	0.75	.03	.001-	97
12	1.50	.50	.001-	140	0.90	.02	.001-	105
26	1.60	.27	.001-	166	1.00	.17	.001-	116
December								
17	1.50	.10	.001-	152	1.40	.23	.001-	127

MALHAM TARN. 1952. All results in milligrams per litre.

2

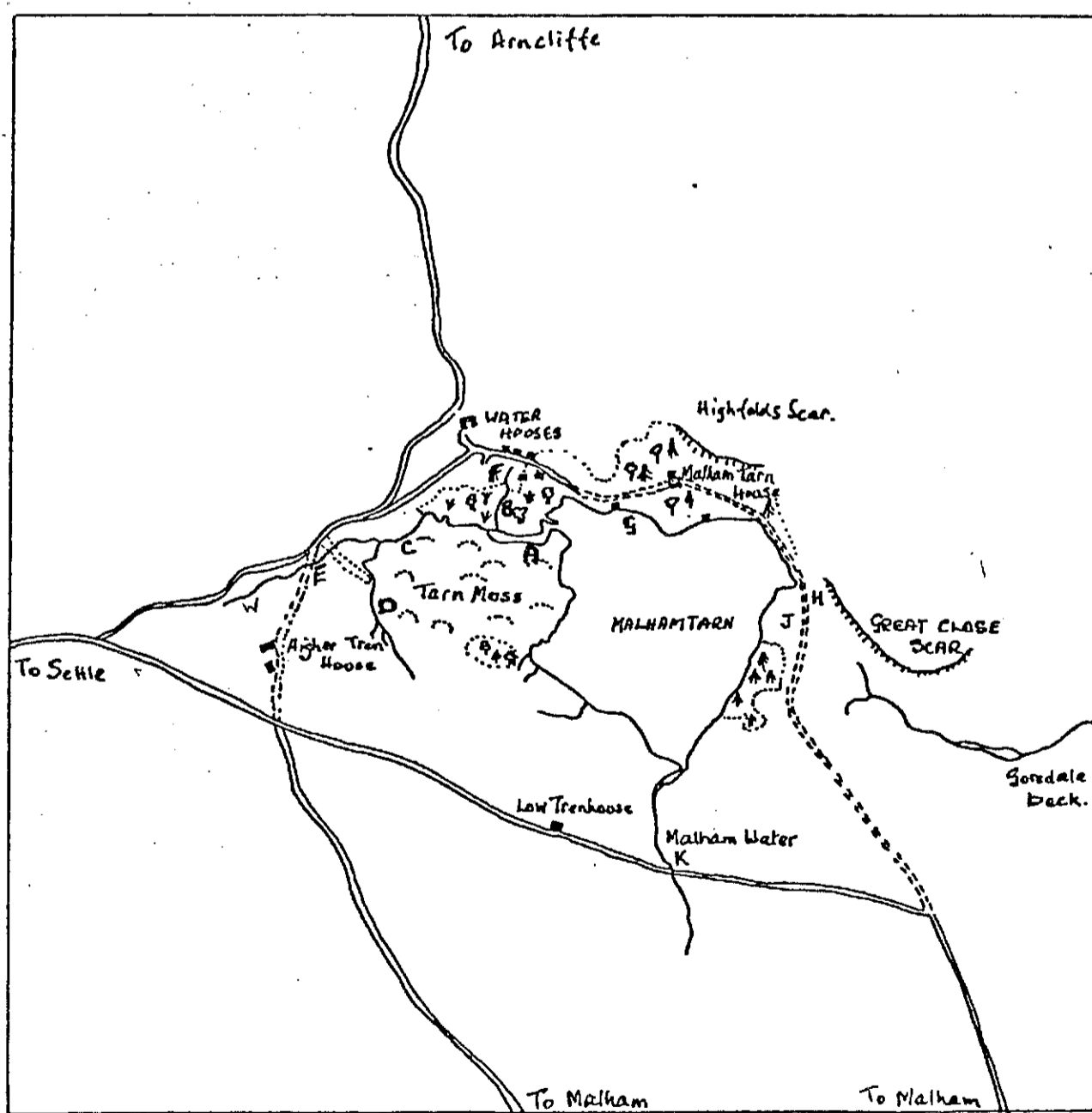
	<u>Inflow sample.</u>				<u>Tarn sample.</u>			
	SiO ₂ .	NO ₃ N.	PO ₄ P.	Alkalinity as CaCO ₃	SiO ₂ .	NO ₃ N.	PO ₄ P.	Alkalinity as CaCO ₃
February								
25	1.30	.29	.001-	136	1.00	.27	.001-	111
March								
10	1.30	.22	.001-	160	0.70	.24	.001-	110
April								
4	1.60	.45	.001-	175	0.60	.20	.001-	112
21	1.10	.30	.001-	164	0.18	.15	.001-	117
May								
19	1.10	.07	.001	176	0.25	.07	.001	116
June								
9	0.90	.03	.001	155	0.22	.02	.001-	98
July								
7	1.00	.09	.001-	173	0.50	.02	.001-	93
25	1.80	.13	.003	198	1.10	.02	.002	87
August								
12	1.90	.05		221	1.40	.02		100
September								
8	1.50	.17	.001	175	0.90	.03	.001	93
October								
6	1.80	.24	.001	203	0.90	.03	.001	108
November								
13	1.70	.24	.001	188	0.90	.08	.001	115
December								
16	1.80	.30	.0015	163	0.90	.09	.0015	129

TABLE 1953. All results in milligrams/litre.

	<u>Inflow sample.</u>				<u>Tarn sample.</u>			
	<u>SiO₂</u>	<u>NO₃N.</u>	<u>PO₄P.</u>	<u>Alkalinity as CaCO₃</u>	<u>SiO₂</u>	<u>NO₃N.</u>	<u>PO₄P.</u>	<u>Alkalinity as CaCO₃</u>
January								
19	1.80	.37	.003	151	1.00	.14	.002	128
March								
4	1.80	.33	.002	177	0.75	.15	.0015	121
April								
9	1.80	.24	.001	136	0.63	.03	.001	120
23	1.00	.25	.001-	156	0.21	.02	.001-	123
May								
6	0.75	.20	.001-	159	0.26	.02-	.001-	121
June								
9	0.86	.20	.0015	155	0.31	.04	.002	102
July								
7	1.80	.17	.001	210	0.90	.03	.001	99
29	1.80	.15	.002	198	1.10	.02	.0025	103
August								
17	1.28	.14	.002	207	0.59	.02	.001	101
September								
7	2.20	.10	.001	231	1.00	.03	.001	121
23	2.10	.03	.001-	220	1.60	.03	.001-	122
October								
19	2.00	.13	.001-	205	1.00	.03	.001-	130
November								
16	2.20	.25	.001	201	1.70	.03	.001	136
December								
14	2.40	.19	.003	158	1.90	.03	.002	142

Analyses by Atomic Absorption Spectrophotometry.

	Ca ⁺⁺ mg/l.	Mg ⁺⁺ mg/l.	Ca/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. (Tarn)	60.0	1.00	60
H.	82.0	0.66	124
J.	92.0	0.84	110
K.	57.0	1.02	56



NO. 1- 117740280 RIVER AIRE AT KALHAN YARD

DATE	TIME	CEL.	PH	TEMP.	61	155	162	172	180	111	117	113	07	82	81	135	85	58	245	215	375	429	9265
						HAZD-	ALK	CHLOR	PHOS-	ARM	PHOS	NITR	SV-T	DO	DO	SS	600-T	TOT.	ZN	CU	CR	NI	CO
						CACOS	TOTAL	IDE	ORPHO	N	ATE-N	ITE-N	ASO-4			105C	ATU	TOT.	TOTAL	TOTAL	TOTAL	TOTAL	TOTAL
						MG/L	MG/L	MG/L	MG/L	MG/L	MG/L	MG/L	MG/L	MG/L	% SAT	MG/L	MG/L	MG/L	MG/L	MG/L	MG/L	MG/L	MG/L
10/18/77	11:00	2	8.1	14.0	112	9	0.1	2	5	<.05	3	12.65	94.38	9	1.6								
10/18/77	11:05	5.5	8.4	109	94	7	<.01	1	0.5	<.05	3	11.9	107.6	8	2.2								
10/18/77	11:10	10.5	8	108	105	5	<.01	3	1	<.05	3	10.9	100.9	5	1.5								
10/18/77	11:15	10.5	8.1	124	118	12	0.1	2	35	<.05	3	12.65	90.57	8	1.6								
10/18/77	11:20	10.5	8.3	124	112	15	<.01	1.5	4	<.05	3	12.7	90.93	2	1.2								
10/18/77	11:25	11.4	8	144	106	10	<.01	1	1	<.05	3	14.1	99.56	1	1.4								
10/18/77	11:30	11.4	7.3	164	116	11	0.2	<.05	35	<.05	3	11.95	95.31	15	2								
10/18/77	11:35	12	8.8	114	116	14	0.5	0.5	0.5	<.05	3	10.15	96.08	1	2								
10/18/77	11:40	11.5	8.8	78	76	64	0.1	<.05	0.5	0.5	3	11.95	126.2	1	0.9								
10/18/77	11:45	16.5	9.2	60	48	13	<.01	1.5	<.05	<.05	3	8.9	89.21	2	2.2								
10/18/77	11:50	14	8.5	66	56	8	0.3	<.5	2.3	<.05	3	9.7	93.01	2	0.8								
10/18/77	11:55	12	8.5	96	76	9	<.01	0.8	13	1	1	14.05	137.7	4	2								
10/18/77	12:00	13	8.7	124	104	11	<.01	<.05	15	<.05	3	11.15	98.43	2	1								
10/18/77	12:05	8.5	7.7	124	119	11	<.02	1.5	1.7	<.05	3	13	93.08	1	1.4								
10/18/77	12:10	5	8.1	134	114	14	<.02	3	2	0.5	3	13.73	99.67	5	1.35								
10/18/77	12:15	1	7.6	142	94	12	<.02	0.9	1	1.6	3	12.48	93.11	5	2.2								
10/18/77	12:20	2	8	114	112	20	<.02	0.2	0.5	1.2	3	12.54	95.86	54	2.2								
10/18/77	12:25	2.9	8.1	130	110	12	<.02	<.05	0.5	2	3	11.85	100.7	1	2.1								
10/18/77	12:30	7	7.6	116	102	15	<.02	<.05	0.5	0.5	3	11.2	106.1	3	1.9								
10/18/77	12:35	10.5	8.1	119	91	9	<.02	0.9	0.5	0.5	3	12	131.9	1	3								
10/18/77	12:40	13.5	8.2	66	60	10	<.02	<.05	0.5	0.5	3	10.2	101.1	2	1.9								
10/18/77	12:45	13.2	8.1	82	81	6	0.2	0.2	0.5	0.5	3	10.1	99.49	1	2.1								
10/18/77	12:50	11	8.1	102	101	8	<.02	0.2	0.5	0.5	3	10.7	100.2	4	2								
10/18/77	12:55	12.9	8.5	122	114	5	0.3	0.8	0.5	0.5	3	10.15	99.31	1	1.1								
10/18/77	13:00	6.5	7.9	132	124	7	<.02	0.8	0.5	0.5	3	10.8	90.7	10	1.7								
10/18/77	13:05	6.5	7.9	134	122	7	<.02	0.8	0.5	0.5	3	10.38	87.84	11	0.65								
10/18/77	13:10	2	7.9	142	124	33	<.02	0.8	0.5	0.5	3	12.8	90.89	1	0.75								
10/18/77	13:15	4.5	8	124	116	9	<.02	0.5	0.6	0.5	3	12.36	98.58	3	2.5								
10/18/77	13:20	1.8	7.6	130	115	8	<.02	0.5	0.42	0.5	3	13.15	97.58	5	3.6								
10/18/77	13:25	8.7	7.4	116	122	10	<.02	0.5	0.5	0.5	3	11.4	99.9	5	2.9								
10/18/77	13:30	13.5	8.2	128	116	12	<.02	0.5	0.5	0.5	3	8.4	83.29	4	1.1								
10/18/77	13:35	10	8.4	120	106	10	<.02	0.8	0.5	0.5	3	10.25	93.82	1	1								
10/18/77	13:40	12.9	8.5	96	83	9	<.02	0.5	0.5	0.5	3	12.6	123.2	1	1.1								
10/18/77	13:45	12.8	8.2	94	78	10	<.02	0.5	0.5	0.5	3	11.2	109.5	5	1.6								
10/18/77	13:50	14.5	8.2	110	91	8	0.7	0.5	0.5	0.5	3	9.78	94.84	2	3.15								
10/18/77	13:55	7.1	8.2	122	109	10	<.02	0.5	0.5	0.5	3	10.9	93.41	1	1.8								
10/18/77	14:00	7.1	8.2	150	120	2	0.6	0.5	0.5	0.5	3	13.91	103.9	5	3								
10/18/77	14:05	3.6	8.2	158	128	6	0.6	0.5	0.5	0.5	3	12.98	94.23	1	1.1								
10/18/77	14:10	4.6	7.7	123	124	6	0.3	0.5	0.5	0.5	3	12.15	97.16	1	1.2								
10/18/77	14:15	4.4	8.2	134	116	7	<.02	0.5	0.5	0.5	3	13.25	105.4	8	1.7								
10/18/77	14:20	7	8	140	116	10	<.02	0.2	0.5	0.5	3	13.7	98.64	8	1.4								
10/18/77	14:25	7.5	7.9	136	130	5	0.1	0.2	0.5	0.5	3	10.9	93.88	1	2.3								
10/18/77	14:30	10.5	8	120	114	9	0.3	0.2	0.5	0.5	3	11	101.8	4	0.8								
10/18/77	14:35	11.5	7.9	124	120	7	<.01	0.2	0.5	0.5	3	10.7	101.4	6	3.2								
10/18/77	14:40	13.6	7.9	132	110	15	0.15	0.5	0.5	0.5	3	9.7	96.39	4	1.75								

Y. P. A. V. S. I. O. N. T. J.

PROGRAM W453/12

WATER ARCHIVE SYSTEM

14.20 14/01/82

PAGE 2
REQUEST NO 1

SPT :- 147740250

NBR :- SD 89390 66180

RIVER AIRE AT MALHAM TARN

SAMPLE	PH	61 HARD- CACO3	156 ALK TOTAL	162 CHLOR IDE	172 PHOS- ORTHO	180 SIO2	182 TEMP.	76 ATM M	111 NITR ATE-N	117 NITR ITE-N	118 DO	82 DO	81 SS 105C	135 COD TOT	92 BOD-T ATU	85 DISSOLVED ORTHOPHOSPHATE	191 M/L
DATE	TIME	MG/L	MG/L	MG/L	MG/L	MG/L	CEL.	MG/L	MG/L	MG/L	MG/L	% SAT	MG/L	MG/L	MG/L	MG/L	MG/L
<-----><----->																	
1009198111	0 8	104	100	10	.02	3	16	<.05	<.03	<.05	9.4	98.3	2		1.7	.01	
0911198111	5 7.0	124	125	4		1	9.3	.03	.2	<.02	10.4		15		.55	.011	
0211198111	15 7.	177	158	7	<.01	1	8	.02	.13	<.01	11.3	95.52	1		1.1	.006	
0112198111	4 6.5	174	134	14	.01	1	3	.04	.28	.02	12.5	92.99	2		1.5	.002	
MEAN		7.475	147.2	129.2	8.75	.0117	1.5	9.075	.0287	.19	.015	10.9	95.6	5		1.212	.0072
S.D.		12.63	34.86	23.96	4.272	.0076	1	5.356	.0085	.0668	.0091	1.519	2.653	6.683		.5072	.0041
MAXIMUM		8.0	177	158	14	.02	3	<.05	<.3	<.05	12.5	98.3	15		1.7	.011	
MINIMUM		7.0	104	100	4	<.01	1	3	.02	.13	<.01	9.4	92.99	1		.55	.002
NO. OF OCCURS.		4	4	4	4	3	4	4	4	4	4	5	4		4	4	
NO. LT.							1		1	1	3						

DATA RECORDED AS BEING LESS THAN LIMIT OF DETECTION - TAKEN AS 1/2 RECORDED VALUE
IF NO. OF LT'S EXCEEDS 30% TREAT DATA WITH CAUTION--IF MORE THAN 50% CONSULT STATISTICS DEPT.

SITE:	PH	PH	H ⁺	Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺	NH ₄ ⁺	me.l ⁻¹				P.P.M.				Σ CATION	Σ ANION	CONDYTY	
									Cl ⁻	SO ₄ ⁻	NO ₃ ⁻	Cu	Fe	Pb	Zn	Al				P
MALHAM TRAIN 20.11.80. MAIN INFLOW SD 8821671	7.55	7.78	0	133	21	3375	77	0	194	240	162	0.01	0.05	0.03	0.06	0.04	0.11	3676	590	365
2	4.2	4.35	45	165	30	150	29	47	176	140	145	0.01	0.63	0.0	0.14	0.25	0.23	466	461	53
3	6.6	7.2	0	133	16	725	38	29	164	142	133	0.01	0.46	0.04	0.10	0.12	0.07	941	439	96
4	7.0	7.9	0	152	16	1800	28	12	166	179	129	0.01	0.09	0.01	0.09	0.11	0.03	2003	474	218
5	4.2	3.8	158	141	14	70	34	47	182	119	152	0.01	0.33	0.0	0.15	0.10	0.05	464	453	53
THRU WEST SLOPE SD 889669	8.1	8.1	0	178	17	2325	71	0	196	222	141	0.01	0.04	0.02	0.04	0.04	0.07	2591	559	265
7	4.8	4.75	18	109	10	150	30	29	118	103	129	0.01	0.57	0.03	0.05	0.03	0.05	346	350	39.5
8	4.2	4.15	71	148	22	148	38	71	166	129	157	0.02	0.35	0.03	0.10	0.11	0.14	498	452	61.5
9	4.3	3.8	158	124	10	33	23	12	146	101	137	0.02	0.13	0.05	0.05	0.04	0.05	360	384	61.5
10	4.5	4.0	100	130	17	48	30	0	142	107	137	0.02	0.24	0.04	0.09	0.10	0.26	325	336	57.5
11	6.8	7.6	0	396	17	950	47	0	366	164	132	0.01	0.13	0.08	0.04	0.04	0.11	1410	682	150
12	5.1	4.15	71	115	35	113	30	0	136	93	194	0.01	0.65	0.06	0.18	0.07	0.30	364	423	46.5
13	5.5	5.05	9	146	16	110	39	0	164	95	286	0.01	0.72	0.05	0.07	0.05	0.61	320	545	33.5

Nitrate concentrations : Malham Tarn 18.1.81
Determined by CEEB

Grid Ref	Site	Concentration $\mu\text{eq l}^{-1}$	mg l^{-1}
887 673	1. North inflow spring	54.35	0.76
881 671	2. North west spring	58.50	0.82
881 670	3. West inflow	51.45	0.72
882 669	4. South inflow	41.45	0.57
888 671	5. Main inflow	36.45	0.51
888 666	6. Spiggot inflow	5.65	0.07
894 670	7. Tarn north shore	46.45	0.65
894 662	8. Tarn outflow	44.35	0.62

NO_3^- determined by sulphuric and perchloric acid NO_2^- absorption method.
ref. Pearsall - Analyst: Vol 92 p. 311 1967

Table 2. Some general chemical characteristics of the springheads of tufa-depositing streams near Malham Tarn.

Springhead	pH	t°C	Ca ⁺⁺ (mM l ⁻¹)	HCO ₃ ⁻ (mM l ⁻¹)	SATCAI.	Date
Cote Gill	7.5	7	1.25	2.20	0.94	5.2.78
Cowside Beck	7.6	7	1.41	2.70	1.01	14.5.73
Gordale Beck	8.2	16	1.87	3.78	1.12	"
Howgill	7.5	8	1.27	2.27	0.94	5.2.78
Howgill tributary	7.4	9	1.77	3.68	1.00	14.5.73
Lower Beck	8.0	7	1.31	2.65	1.06	"
Waterfall Beck	7.5	6	1.37	2.74	1.00	"

Table 3. Detailed analyses of tufa-depositing waters near Malham Tarn (springheads, excluding Malham Tarn) ($\mu\text{M l}^{-1}$)

Component	Malham Tarn (mid-lake)	Gordale Beck	Howgill tributary	Waterfall Beck
Ca ⁺⁺	1140	1690	1755	1299
Mg ⁺⁺	38	31	85	28
Na ⁺	320	164	261	153
K ⁺	16	24	15	7
HCO ₃ ⁻	2040	3150	3540	2650
CO ₃ ²⁻	37	28	24	7
CO ₂ +H ₂ CO ₃	11	28	48	99
P (total reactive)	0.09	0.09	0.01	0.04
SO ₄ ²⁻	162	148	154	120
NO ₃ ⁻	0.07	0.06	0.10	0.03
pH	8.5	8.2	8.1	7.5
t°C	9	15	10	6
date	14.5.73	13.5.73	13.5.73	13.5.73

dioxide partial pressure (i.e. concentration) in the soil atmosphere. This gas reacts with water to form carbonic acid, the principal agent of limestone solution (see Appendix 1). South-facing catchments will tend to have warmer, bacteriologically more active soils resulting in a calcium-rich groundwater and it is interesting to note that the waters of Gordale Beck, rising from south-facing slopes, are significantly harder than those of north-facing Waterfall Beck, nearby (Fig. 2, Table 3).

Detailed studies of Waterfall Beck (Fig. 5) and Gordale show that the concentrations of calcium and total carbon dioxide (C_t , Appendix 1), decrease downstream. This fall is attributed to a diffusional loss of carbon dioxide from the water to the atmosphere, and photosynthetic uptake by aquatic plants. This results in the supersaturation of the waters with calcite since much of the carbon dioxide gained by the water from the carbon dioxide rich soil atmosphere is lost once the waters regain contact with the air. There are therefore three carbon dioxide "sinks", or removal processes, for these waters, (a) the atmosphere, (b) photosynthesis and (c) calcite precipitation. It is possible to estimate (a + b) and c separately since calcium carbonate precipitation and the fall in C_t can be measured independently (Appendix 2). For example, the data obtained for 17.8.1974 (Figs 5 and 6) show a total down-