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The Stable Isotope analyses of rainfall and runoff at Plynlimon

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INTRODUCTION

As part of the establishment of a stable isotope laboratory at Wallingford exploratory monitoring at sites of special scientific interest was proposed. Its main purpose was to give direction and foundation to further studies into isotopes in the hydrological cycle. Plynlimon was chosen as a site for preliminary studies. However, the initial monitoring programme was rapidly overtaken by specific project work resulting in long delays to this early IH investigation.

The location of the area being studied was centred on the Institute of Hydrology research catchment, Plynlimon in mid Wales. This is an area of high rainfall, the climate mainly determined by the prevailing westerly winds. The catchment is approximately 20 km east of the coastline. Rainfall samples were collected on a daily and monthly basis during March and April 1978. In addition, collection of runoff water from the river Hafren was taken every day. Four sites were chosen for rainfall investigations, although at present only three sites, Tanllwyth, Dolydd and LLanidloes have been analysed in any detail.

The samples were analysed for their stable oxygen and hydrogen isotopes. Analysis was by mass spectrometry at the IGS/IH stable isotope laboratory, Wallingford.

The areas of investigation were as follows:

(i) Daily and monthly samples of rain from Tanllwyth met site, to establish a correlation between a daily weighted isotopic mean and monthly isotope values. Tanllwyth also provides a comprehensive collection of meteorological data, available for the period of this investigation.

(ii) Isotopic correlation with altitude. The elevation of the sites are as follows:

Tanllwyth	360 m a.o.d.
Dolydd	305 m a.o.d.
LLanidloes	198 m a.o.d.

(iii) Comparison of forest canopy throughfall with unimpeded ground level collection to observe possible shifts in isotopic composition by interception of precipitation by forested areas.

(iv) Correlation between $\delta^{18}O$ and temperature.

(v) Stream runoff behaviour employing stable isotopes, collected on a daily basis from the river Hafren.

ANALYTICAL METHODS

The samples were analysed for $\delta^{18}O$ in CO_2 and $\delta^{2}H$ in H_2 using standard techniques detailed in Darling and Bath (1979).

Hydrogen samples were prepared using a V G Micromass UR2 extraction line. A detailed method of operation for this line may be found in Stable Isotope Technical Report No 8 (Brunsdon and Bath, 1981).

Carbon dioxide gas equilibration was achieved by isotopic exchange between the CO_2 and a 5 ml water sample. Complete equilibration was reached in 18 hours within a sealed flask at 25^{O}C.

Analysis of the respective gases were performed by a V G Micromass 602E dual analyser mass spectrometer.

The laboratory working standard, Wallingford tap water (W T W), was prepared and analysed together with the samples. Both working standards and samples were compared for isotopic composition against an arbitrary reference gas. The calibration between the international standard SMOW (Standard Mean Ocean Water) and W T W is known, as is a calibration factor used to correct for instrumental bias on slope between SMOW and SLAP. SLAP (Standard Light Antarctic Precipitation) is a standard very depleted in ^{18}O and ^{2}H.

RESULTS

From a study of this kind a large number of values are obtained for several measurable parameters. Tabulation of all the data with its corresponding inter-relationships is a problem and a perfect solution is difficult to obtain. The following tables and graphs, it is hoped, convey the necessary aspects of the study.

Analytical data for $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios are presented in the conventional δ-notation, where, for example:

$$\delta^{18}O = \left[\frac{(^{18}O/^{16}O)\ \text{sample}}{(^{18}O/^{16}O)\ \text{standard}} - 1 \right] \times 1000 \text{ per mil } (^{o}/oo)$$

Table 1 lists isotopic data for daily (March 1978) and monthly rainfall collections at the 3 sites. Detailed daily meteorological information is compared with the daily isotope data at Tanllwyth in Table 2. Isotopic composition of runoff sampled at Hafren is shown in Table 3. Figures 1 and 2 also present these data in conventional diagrams.

With reference to the isotope data the errors on the values obtained represent the confidence which the laboratory can place on that particular analytical value. Errors which cannot be accounted for are those which may occur as a result of collection and transportation of the sample to the laboratory.

The accuracy of the oxygen preparation method is well established and limits of precision apply to single determination of $\delta^{18}O$. The hydrogen preparation technique is not so reproducible. For $\delta^{2}H$ analyses replicate determinations are carried out, at least two, in order to eliminate spurious results.

DISCUSSION

1. Daily versus monthly samples

Tanllwyth provides the most comprehensive set of data from the sites studied. Daily samples, not collected under oil, were obtained using a Standard Meteorological Office daily gauge. Rainfall data are given in Figure 3. Octapent raingauges were used for the monthly collections, again without oil, to investigate if samples underwent isotopic fractionation.

A set of data from Tanllwyth has been processed and gives the following comparisons for March 1978:

	$\delta^{18}O$ ‰	$\delta^{2}H$ ‰
Ground level gauge, monthly	- 6.6	- 43
Daily gauge, weighted, monthly mean	- 6.5	- 42

There is thus a good correlation between monthly and weighted mean of daily data. This indicates the monthly sample has not been significantly fractionated over the collection period. High, consistent rainfall amounts and a low mean monthly temperature will all have contributed to the reduction of evaporative effects and consequently any fractionation. The follow on work from this single months experiment should cover months having a spread of rainfall amount and higher temperatures. If possible, simultaneous collections with and without an oil film should be taken. This would help to establish where and when an oil film is necessary and whether any analytical problems arise as a result of using oil.

Altitudinal variation

Correlation of isotopes with altitude is due mostly to temperature differences and their effect on condensation fractionation, although the process is further complicated by meteorological and topographical effects. Recognition of the altitude component is thus difficult and is essentially unknown for the U.K. At Plynlimon the difference in elevation between the three sites is not large. This makes isolation of the altitude component more difficult, as alternative processes could mask any small isotopic change due to elevation.

Samples for 6 days were analysed from all three sites (12-15, and 19-20 March). These data are plotted in Fig.4. Isotopically lighter water is found at the higher altitudes. Numerically the set of data breaks down as follows.

	Mean $\Delta\delta$	$\delta^{18}O$ ‰ /100 m
Mean Variation (Tanllwyth - Dolydd)	- 0.20	- 0.36
Mean Variation (Tanllwyth - Llanidloes)	1.30	- 0.80
Mean Variation (Dolydd - Llanidloes)	1.10	- 1.03

Studies carried out in Europe into similar altitude effects have $\delta^{18}O$ ‰/100 m values in the range - 0.16 to - 0.4 (Siegenthaler and Oeschger, 1980). Apart from the Tanllwyth/Dolydd variation the values above lie well outside this range. The most likely explanation of this is other factors having far more influence over composition than the temperature related altitude effect. Long term data are required to allow a fuller statistical analysis of these variations.

Siegenthaler and Oeschger (1980) have recently completed a ten year investigation into correlation of ^{18}O with altitude and temperature. Their study was concerned with an area of central and westernSwitzerland where station elevations vary considerably. A value of - 0.26 $\delta^{18}O$ ‰/100 m was obtained from one group of sites. It should, however, be noted that these values were based on averages from each site built up over at least 18 months. Also to be remembered with the Swiss Study and several others in Europe, is the continental nature of air-mass movement and precipitation.

3. Temperature Dependence

Correlation of rainfall-weighted temperatures against variations in ^{18}O,(Fig 5),show little relationship over a month's sampling. There is perhaps more value to be gained by plotting monthly means over a year's monitoring. Dansgaard (1964) has developed a global relationship based on a similar criterion, $\delta^{18}O = 0.7\ t - 13.65$ ‰ . It would be interesting to see how this relationship performs with a more intensive investigation at Plynlimon.

4. $\delta^{18}O$-$\delta^{2}H$ Relationship

An empirical linear relationship between $\delta^{18}O$ and $\delta^{2}H$ is now well established, having resulted from earlier work by Craig (1961) and Dansgaard (1964). In effect the linear relationship remains nearly constant across a range of locations and conditions worldwide and is $\delta^{2}H = 8\,\delta^{18}O + 10$. By applying linear regression to the Plynlimon data in Figs 1 & 2, a close agreement can be seen between this and Dansgaard's World Meteoric Line of $\delta^{2}H = 8\ \delta^{18}O + 10$. The numerical results are given below.

Site	Slope	Intercept	Correlation(r)	
Tanllwyth	7.9	10.0	0.96	23
Dolydd	8.0	11.4	0.98	8
Llanidloes	9.6	15.2	0.98	6
World Meteoric	8	10		

5. Comparison of open and throughfall collections

Comparisons of monthly throughfall precipitation and monthly unimpeded, ground level rainfall (Table 1), have provided conflicting results over the two months studied. There is close agreement of isotopic concentration for March but clearly isotopic enrichment of the throughfall during April. It could be beneficial to investigate further such throughfall effects on isotope composition in relation to both interception within the canopy and to the characteristics of recharge beneath a forest.

6. Rainfall-runoff relationships

Data is available from samples obtained directly from the river Hafren on a daily basis for the month of March. Due to pressure on mass spectrometer time, only $\delta^{2}H$ analyses are at present available (Table 3). This is not, however, a serious limitation and much can be concluded from the analyses obtained.

Apart from some minor deviations, the isotope composition of runoff remains constant throughout the month. This implies that the process is part of a well mixed system. With a mean runoff δ^2H of - 46 ‰ and a mean input (Tanllwyth) δ^2H of - 43 ‰, the runoff is ^2H depleted with respect to input during March. As March follows months where mean monthly rainfall is likely to be depleted in ^2H, a possible explanation is that some runoff observed resulted from recharge during previous months. With much of the area surrounding the Hafren being largely peat, a high quantity of surface storage is possible.

The minor deviations in ^2H enrichment over the month although small, show a limited relationship to a runoff flow profile: it may be a useful extension to the investigations to include some detailed collections of runoff during a storm event. This could take the form of automatic samplers, triggered during a major event and sampling every hour for up to 24 hours.

SUMMARY

The various aspects discussed in this report provide background data on which more detailed investigations can be based. This study was of an exploratory nature and as such does not provide detailed answers or comprehensive data. Its main purpose is to give direction and foundation to further studies into isotopes in the hydrological cycle.

Below is a brief description of the main conclusions drawn from the project.

(a) Use of a monthly raingauge sample collector is probably a satisfactory means of obtaining a monthly mean isotopic value, an alternative to weighted daily collections, in cool and wet months.

(b) Using an oil film under which rainfall samples are collected does not appear to be necessary for monthly periods having low mean temperatures and high rainfall amounts.

(c) There does seem to be a correlation between altitude and isotope value; however, other climatic and topographical effects seem to mask the accepted relation at Plynlimon.

(d) From data available no correlation of ^{18}O with temperature on a daily basis can be seen. There is, however, the possibility of a mean monthly or mean annual relationship existing.

(e) The monthly throughfall isotope values are conflicting for the two months studies and no satisfactory conclusions can be made concerning isotopic differences between throughfall and rainfall.

(f) Runoff in the Hafren exhibits little isotopic variation in contrast to the daily variations in corresponding rainfall. Storage seems therefore to be an important element in the generation of runoff. Short-term processes are implied.

REFERENCES

Brunsdon, A.P. & Bath, A.H. 1981. Operation of the VG-MM5010 (UR2) Preparation line for conversion of H_2O to H_2 for isotopic analysis. Stable isotope technical report No.8.

Craig, H. 1961 Isotopic variations in meteoric waters, Science, 133, 1702.

Dansgaard, W. 1964 Stable isotopes in precipitation Tellus, 16(4), 436.

Darling, G. & Bath, A.H. 1979 Mass spectrometer operation and measurement of $^{18}O/^{16}O$ and $^{2}H/^{1}H$ in water samples. IGS Report WD/ST/79/7.

Siegenthaler, U. & Oeschger, H. 1980 Correlation of ^{18}O in precipitation with temperature and altitude Nature, Vol. 285, No. 5763, pp 314-317.

TABLE 1 Stable oxygen and hydrogen isotope analyses of rainfall, Plynlimon Project

Tanllwyth March 78

SAMPLE NO	DATE	RAINFALL (MM)	$\delta^{18}O$ ‰	$\delta^{2}H$ ‰
TM 1	1/3/78	5.1	-6.8 ± 0.1	-45 ± 1
TM 2	2/3/78	3.3	-10.9 ± 0.1	-80 ± 2
TM 7	7/3/78	13.4	-5.3 ± 0.1	-34 ± 1
TM 9	9/3/78	1.2	-5.2 ± 0.1	-41 ± 2
TM 11	11/3/78	1.8	-3.6 ± 0.1	-20 ± 2
TM 12	12/3/78	2.6	-6.2 ± 0.1	-34 ± 2
TM 13	13/3/78	29.2	-8.8 ± 0.1	-64 ± 2
TM 14	14/3/78	44.9	-8.3 ± 0.1	-51 ± 2
TM 15	15/3/78	4.4	-5.7 ± 0.1	-27 ± 2
TM 16	16/3/78	1.6	-8.6 ± 0.1	-52 ± 2
TM 18	18/3/78	1.1	-3.3 ± 0.1	-11 ± 2
TM 19	19/3/78	45.1	-4.6 ± 0.1	-30 ± 2
TM 20	20/3/78	20.2	-7.8 ± 0.1	-53 ± 2
TM 21	21/3/78	4.5	-5.1 ± 0.1	-29 ± 2
TM 22	22/3/78	16.5	-4.8 ± 0.1	-27 ± 1
TM 23	23/3/78	11.1	-9.1 ± 0.1	-55 ± 1
TM 24	24/3/78	4.9	-3.4 ± 0.1	-14 ± 2
TM 25	25/3/78	11.6	-6.2 ± 0.1	-38 ± 2
TM 26	26/3/78	30.6	-4.9 ± 0.1	-35 ± 1
TM 28	28/3/78	6.6	-5.8 ± 0.1	-41 ± 2
TM 29	29/3/78	5.0	-6.4 ± 0.1	-33 ± 1
TM 30	30/3/78	2.3	-7.4 ± 0.1	-48 ± 1
TM 31	31/3/78	3.5	-8.7 ± 0.1	-63 ± 2
*TGM	MONTHLY GAUGE		-6.6 ± 0.1	-43 ± 2
*TTM	MONTHLY GAUGE		-6.8 ± 0.1	-43 ± 1

Tanllwyth April 78

*TGA	MONTHLY GAUGE		-8.7 ± 0.1	-58 ± 2
*TTA	MONTHLY GAUGE		-3.5 ± 0.1	-50 ± 1

*TG = TANLLWYTH GROUND LEVEL

*TT = TANLLWYTH THROUGHFALL

TABLE 1 (Cont'd)

Dolydd March 78

SAMPLE NO	DATE	RAINFALL (MM)	$\delta^{18}O$ ‰	$\delta^{2}H$ ‰
DM 12	12/3/78	N/A	-6.2 ± 0.1	-36 ± 1
DM 13	13/3/78	N/A	-9.0 ± 0.1	-66 ± 2
DM 14	14/3/78	N/A	-7.9 ± 0.1	-51 ± 2
DM 15	15/3/78	N/A	-5.3 ± 0.1	-27 ± 2
DM 16	16/3/78	N/A	-8.4 ± 0.1	-53 ± 1
DM 18	18/3/78	N/A	-3.1 ± 0.1	-14 ± 2
DM 19	19/3/78	N/A	-4.1 ± 0.1	-26 ± 1
DM 20	20/3/78	N/A	-7.6 ± 0.1	-51 ± 1

Llanidloes March 78

SAMPLE NO	DATE	RAINFALL (MM)	$\delta^{18}O$ ‰	$\delta^{2}H$ ‰
LM 12	12/3/78	N/A	-4.7 ± 0.1	-28 ± 2
LM 13	13/3/78	9.7	-7.8 ± 0.1	-61 ± 2
LM 14	14/3/78	25.0	-6.5 ± 0.1	-49 ± 1
LM 15	15/3/78	3.0	-4.3 ± 0.1	-21 ± 1
LM 19	19/3/78	20.9	-3.3 ± 0.1	-21 ± 1
LM 20	20/3/78	12.0	-7.2 ± 0.1	-52 ± 1

TABLE 2 Stable Isotope and Meteorological data, for Tanllwyth site, March 1978

DATE	$\delta^{18}O$	$\delta^{2}H$	RAINFALL	TEMPERATURE		WIND SPEED & DIRECTION	
	(‰)	(‰)	(MM)	MAX °C	MIN °C	(MPH)	(DEG)
1/3	-6.8	-45	5.1	7.7	5.5	9	130°
2/3	-10.9	-80	3.3	6.1	2.9	2	170°
7/3	-5.3	-34	13.4	8.5	0.0	3	250°
9/3	-5.2	-41	1.2	9.5	-2.3	0	000°
11/3	-3.6	-20	1.8	8.1	2.0	3	270°
12/3	-6.2	-34	2.6	6.7	4.9	4	240°
13/3	-8.8	-64	29.2	7.1	1.6	4	180°
14/3	-8.3	-51	44.9	6.7	4.4	8	270°
15/3	-5.7	-27	4.4	5.9	2.3	8	300°
16/3	-8.6	-52	1.6	4.5	-1.1	7	270°
18/3	-3.3	-11	1.1	6.5	-5.8	2	220°
19/3	-4.6	-30	45.1	8.1	1.2	7	170°
20/3	-7.8	-53	20.2	4.8	1.4	4	250°
21/3	-5.1	-29	4.5	6.1	0.8	8	300°
22/3	-4.8	-27	16.5	7.9	2.1	11	180°
23/3	-9.1	-55	11.1	3.9	0.6	8	270°
24/3	-3.4	-14	4.9	7.3	0.4	7	310°
25/3	-6.2	-38	11.6	7.9	3.6	6	270°
26/3	-4.9	-35	30.6	8.4	0.2	6	270°
28/3	-5.8	-41	6.6	9.3	5.2	8	260°
29/3	-6.4	-33	5.0	8.5	3.8	5	300°
30/3	-7.4	-48	2.3	8.0	2.2	3	260°
31/3	-8.7	-62	3.5	7.2	-1.4	4	090°

TABLE 3 <u>Hafren runoff and Isotope data for March 1978</u>

DAY	RAINFALL (MM)	RUNOFF (MM)	δ^2H RUNOFF (‰) ±1	
1/3/78	5.1	6.1	-49	
2/3/78	3.3	5.4	-48	
3/3/78		4.5	-46	
4/3/78		3.8	-45	
5/3/78		3.4	-36; -40	? on analysis
6/3/78		3.0	-45	
7/3/78	13.4	3.6*	-47	
8/3/78		4.7*	-46	
9/3/78	1.2	3.5*	-43	
10/3/78		3.1*	-45	
11/3/78	1.8	2.9*	-45	
12/3/78	2.6	3.1*	-40	
13/3/78	29.2	8.5*	-44	
14/3/78	44.9	26.8*	-50	
15/3/78	4.4	11.9*	-49	
16/3/78	1.6	6.9*	-49	
17/3/78		4.0*	-46	
18/3/78	1.1	3.3*		
19/3/78	45.1	17.3*	-44	
20/3/78	20.2	19.7*	-48	
21/3/78	4.5	7.9*	-45	
22/3/78	16.5	9.7	-46	
23/3/78	11.1	8.3	-45	
24/3/78	4.9	7.8	-45	
25/3/78	11.6	8.6	-46	
26/3/78	30.6	11.2	-47	
27/3/78		11.8	-42	
28/3/78	6.6	8.0	-44	
29/3/78	5.0	6.3	-46	
30/3/78	2.3	5.0	-46	
31/3/78	3.5	4.6	-45	

* Estimated from Severn due to recorder failure

FIG 1 PLYNLIMON DAILY RAINFALL ISOTOPE COMPOSITIONS 3/78
LLANIDLOES=+ DOLYDD=* TANLLEWYTH=X REGRES=WORLD MET LINE

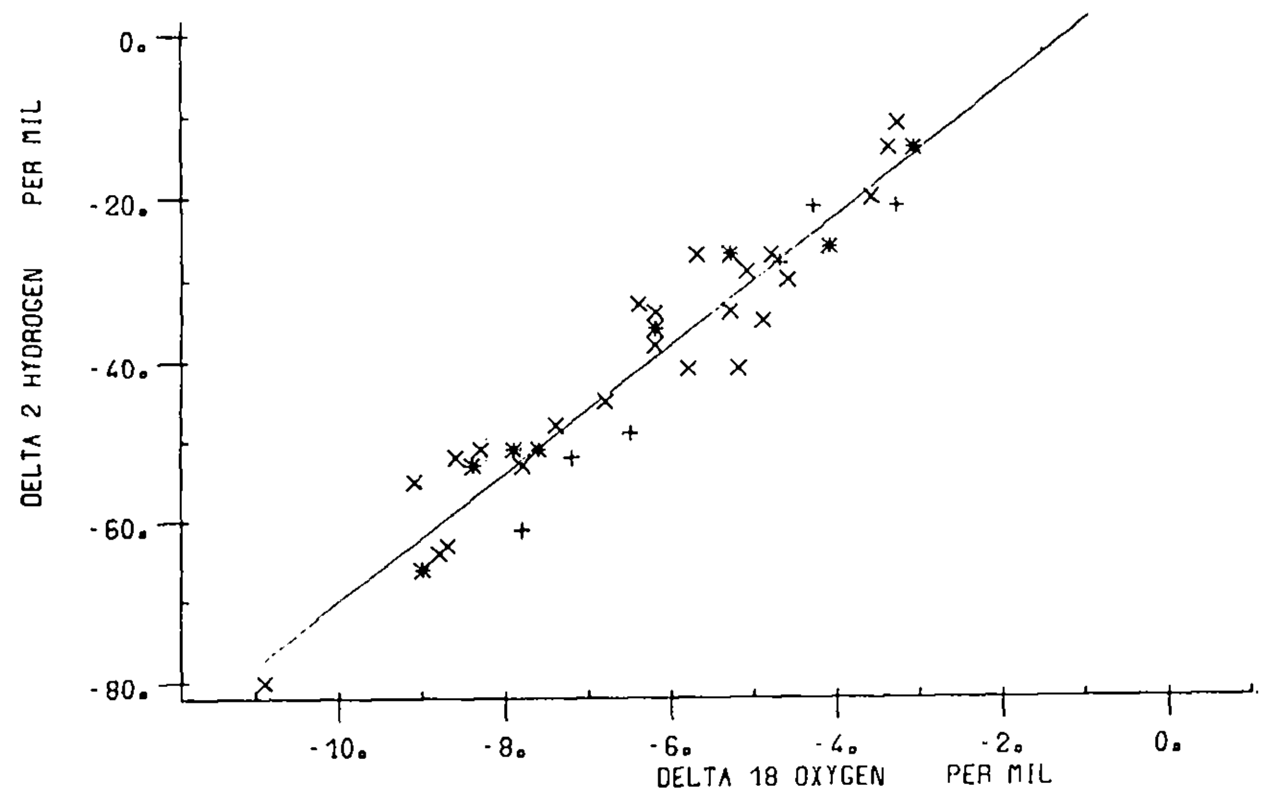


FIG 2 TANLLEWYTH RAINFALL ISOTOPE COMPOSITIONS 3/78

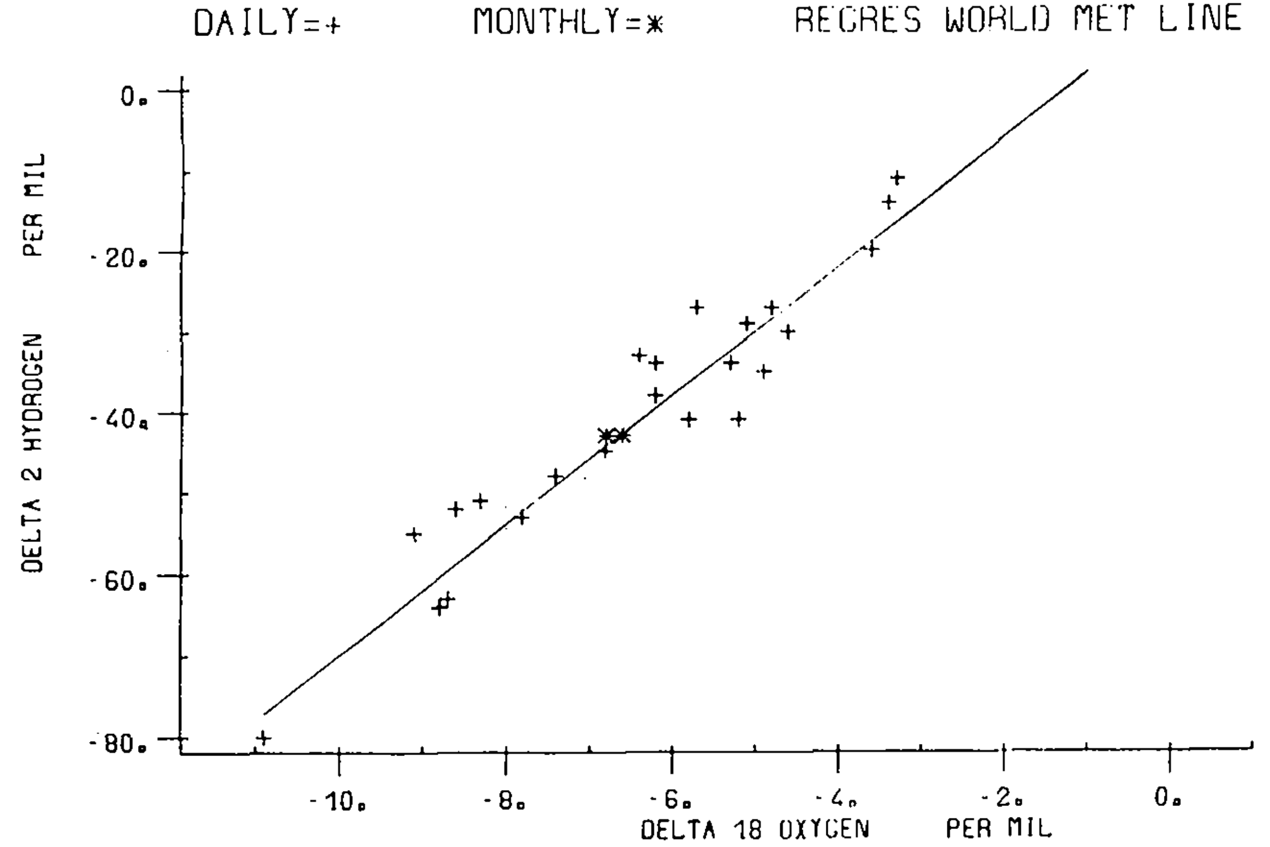


FIG 3 TANLLEWYTH RAINFALL AMOUNTS 3/78

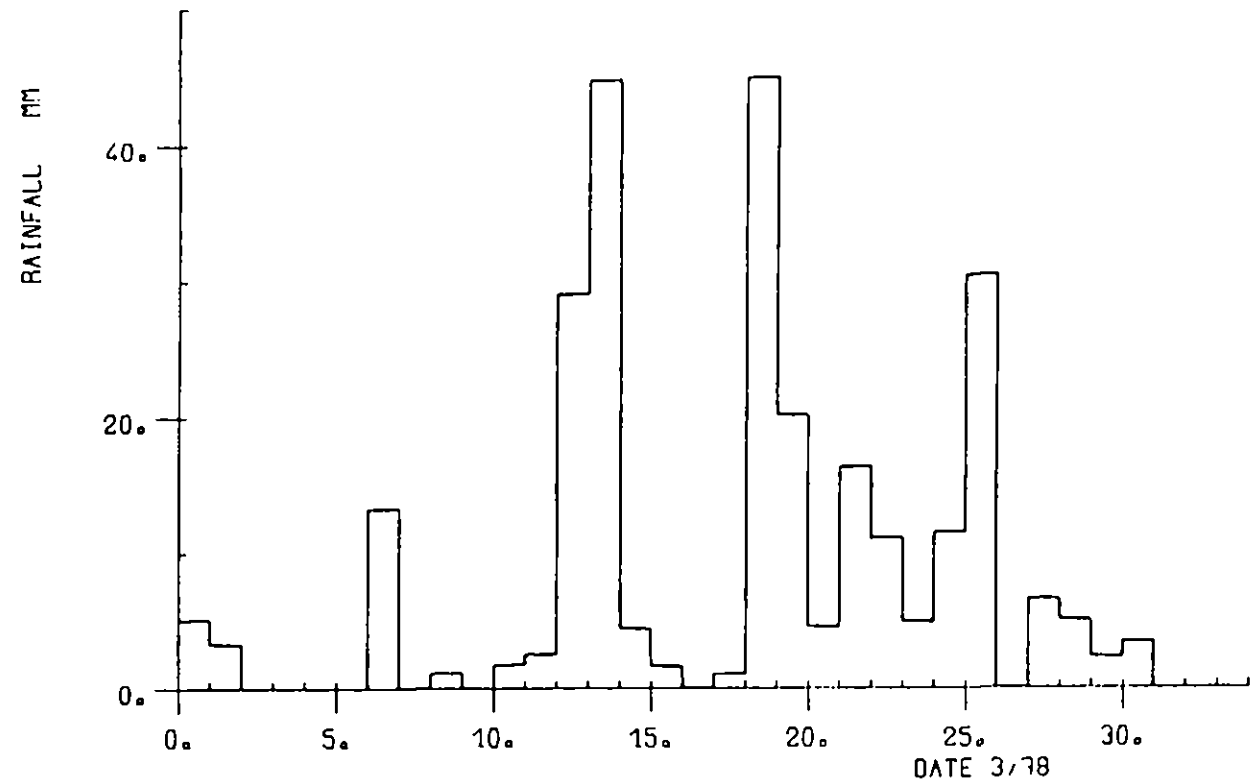


FIG 4 CORRELATION OF 18 OXYGEN WITH ALTITUDE 3/78
TANLLEWYTH=+ DOLYDD=* LLANIDLOES=X

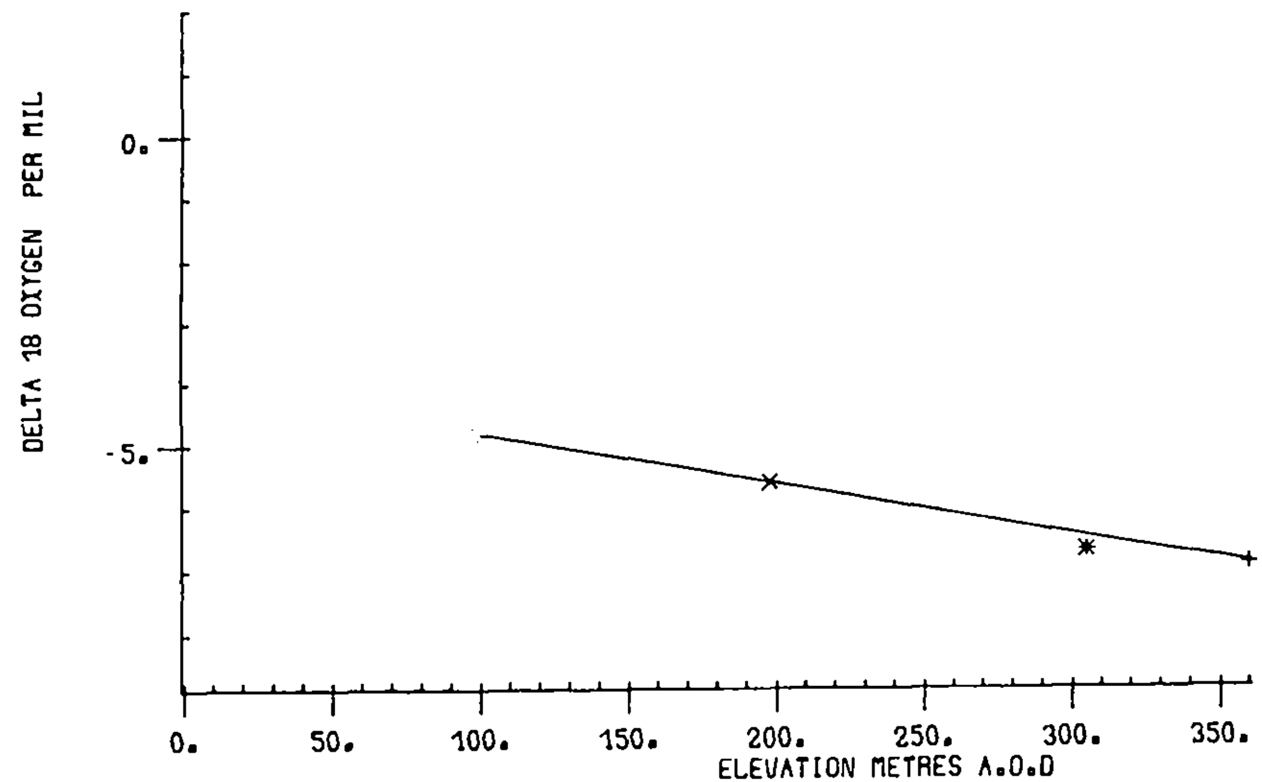
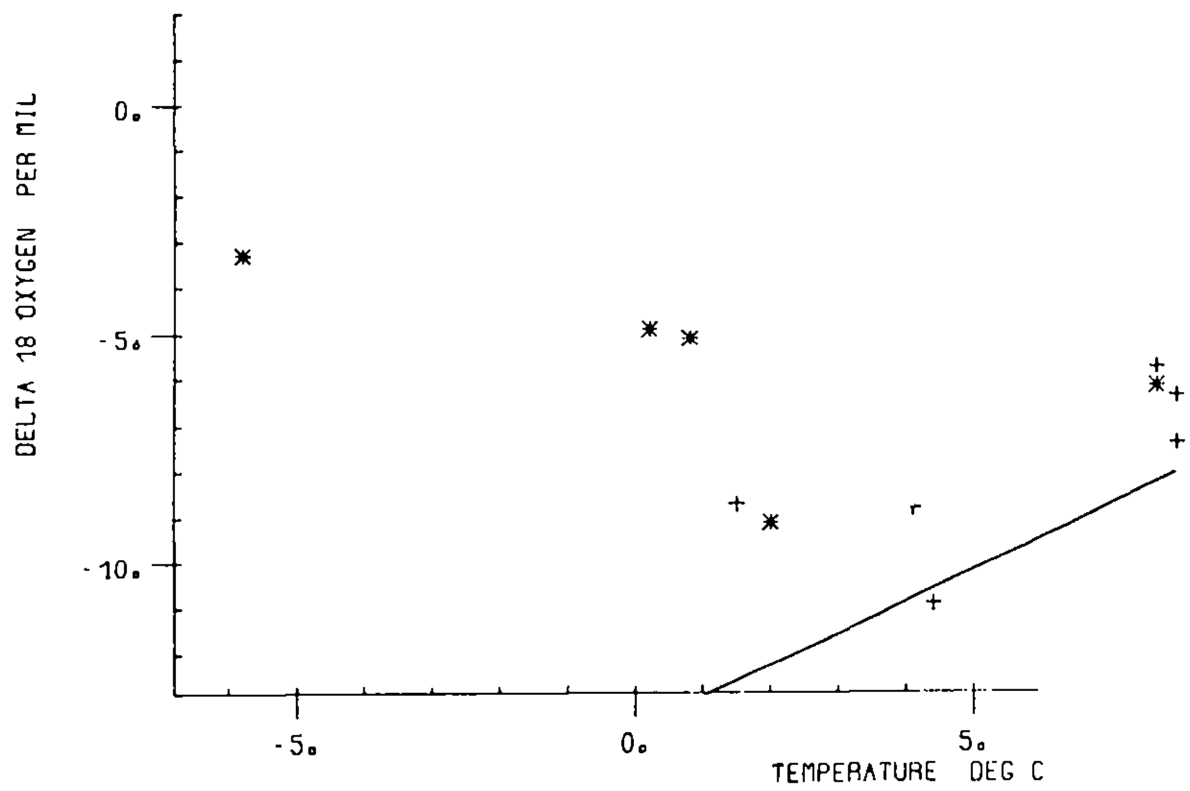


FIG 5 TANLLEWYTH 18 OX VS RAINFALL WEIGHTED TEMP 3/78
RAIN=+ SNOW/ICE MELT=* MEAN=X REGRESS DANSGAARD GLOBAL



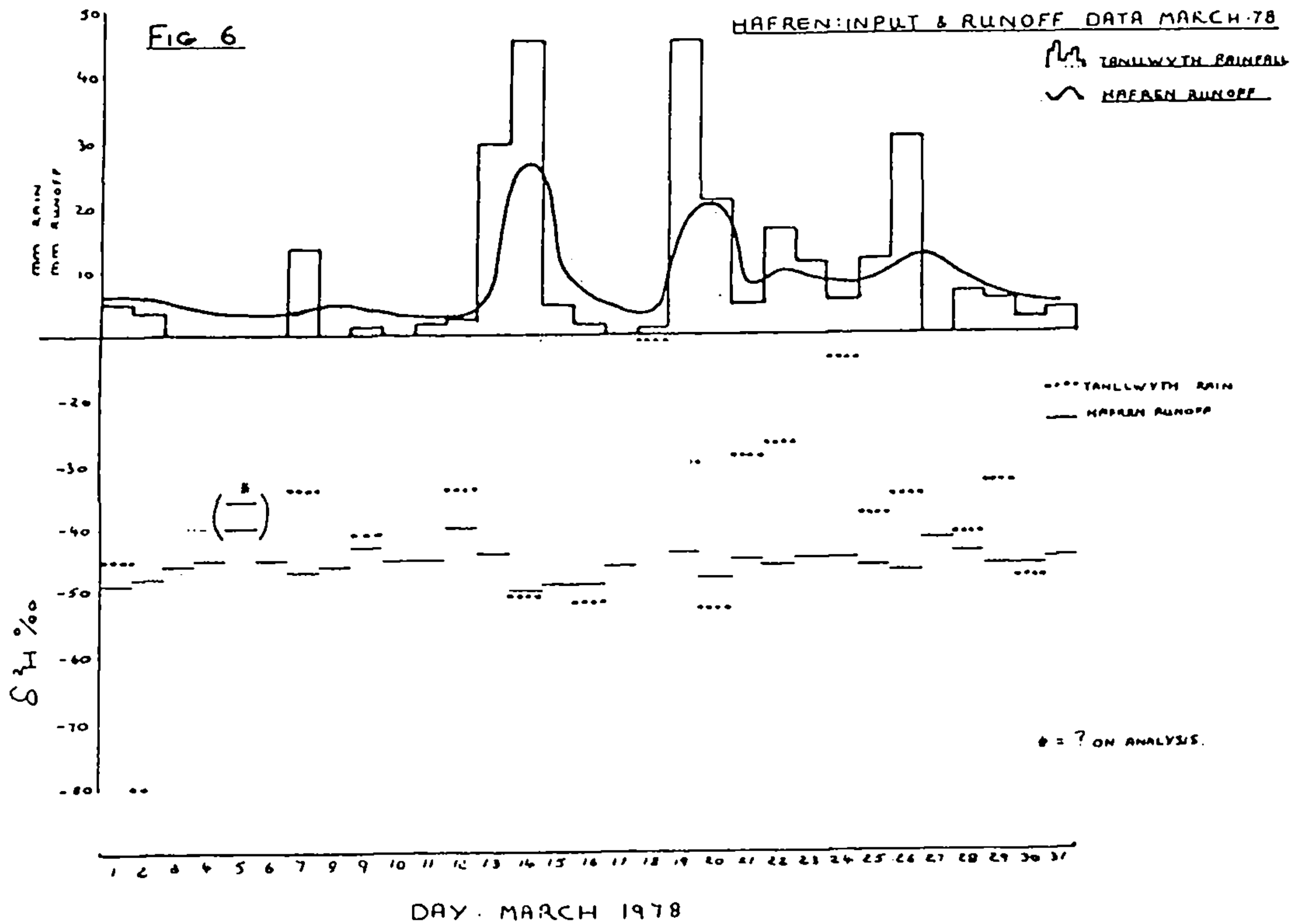
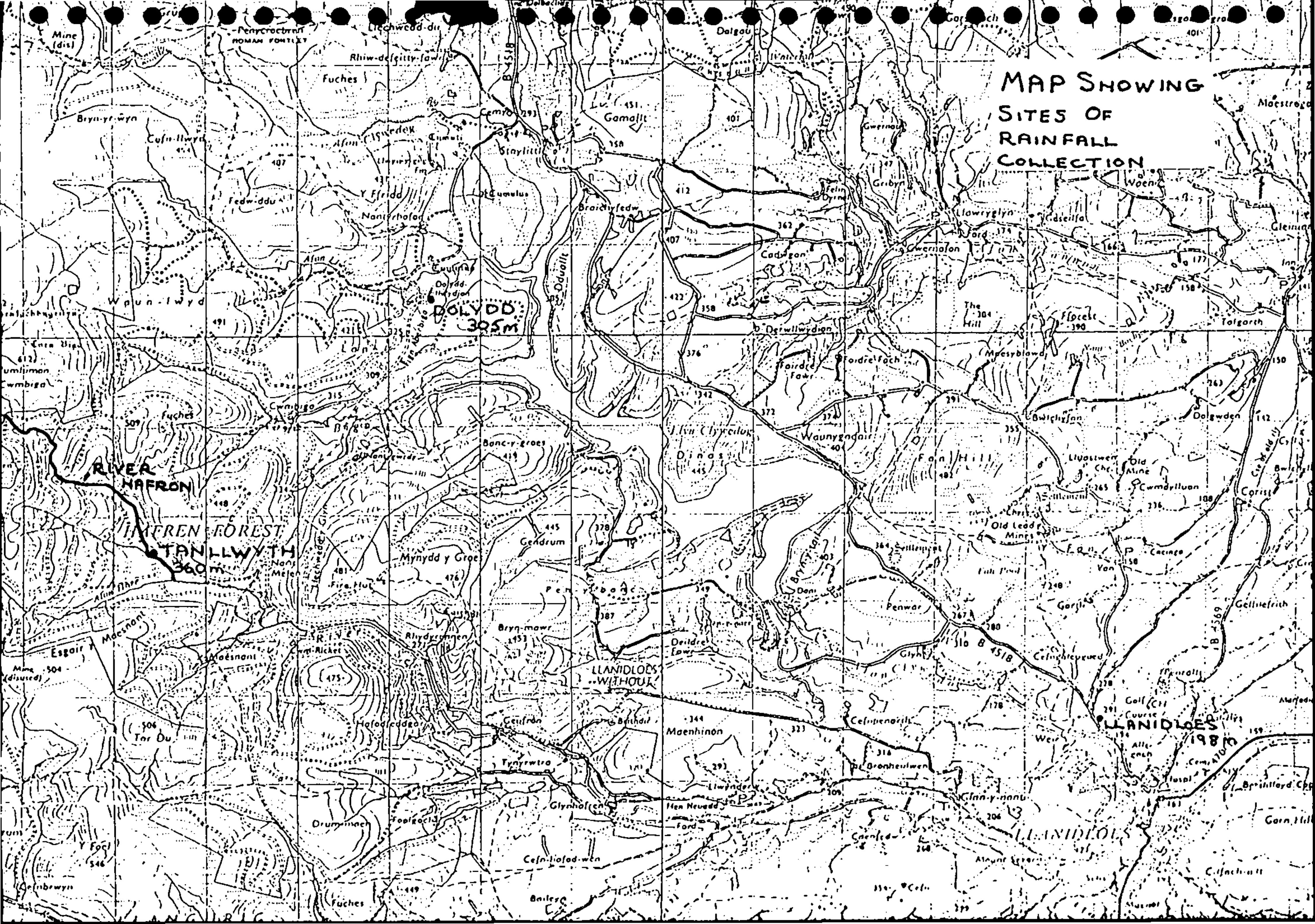

HAFREN: INPUT & RUNOFF DATA MARCH ·78
TANLLWYTH RAINFALL
HAFREN RUNOFF
mm RAIN
mm RUNOFF
50
40
30
20
10
-20
-30
-40
-50
-60
-70
-80
δ ²H ‰
TANLLWYTH RAIN
HAFREN RUNOFF
* = ? ON ANALYSIS.
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31
DAY · MARCH 1978

FIG 6


MAP SHOWING
SITES OF
RAINFALL
COLLECTION
DOLYDD
305m
RIVER
HAFRON
TANLLWYTH
360m
LLANIDLOES
198m