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ITE PROJECT 925

Interim Report to the Department of the Environment

THE EFFECT OF ALTITUDE AND OCCULT PRECIPITATION  
ON ACID DEPOSITION AT GREAT DUN FELL, CUMBRIA

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## 1 INTRODUCTION

The project consists of two studies, the first a collaboration between the Institute of Terrestrial Ecology (ITE) and the University of Manchester Institute of Science and Technology (UMIST) to investigate the dependence of cloud and precipitation chemistry on altitude, and the second a collaboration between UMIST and the Atomic Energy Research Establishment (AERE) Harwell to study liquid phase oxidation of SO<sub>2</sub>, air and cloud water chemistry on Great Dun Fell. Both aspects of the project include modelling studies to interpret the field measurements and to develop an understanding of atmospheric chemistry and deposition procession in the uplands. (The work of AERE was supported by separate funding from the Department of the Environment).

The first progress report on the Great Dun Fell project (April 1985) included examples of the early measurements and results of the early modelling studies. This intermediate report is not designed to provide a comprehensive account of the work so far; this will be provided in the final report to be made in 1987. Rather, the report outlines progress so far on the two main studies and a detailed account of a precipitation event for which field measurements of rainfall and cloud chemistry variations with altitude are compared with the results of modelling work.

The measurement programme of the project now includes 4 field campaigns on and around Great Dun Fell. The first, during autumn 1984, was restricted mainly to rainfall composition measurements with cloud microphysical back-up data. Campaigns in spring and autumn 1985 were much more extensive, and furnish the main source of information for this progress report. During these two campaigns, data recorded included rain and cloud water composition

at up to 8 different heights on Great Dun Fell, measurements of cloud microphysical properties and meteorology at 2 heights, concentrations of  $O_2$ ,  $SO_2$ ,  $O_3$ ,  $NO_2$ , and aerosol, and measurements of  $H_2O_2$  concentrations in precipitation, cloud water and air at up to 4 different locations on Great Dun Fell.

The chemical analyses for major ions in precipitation and cloud water samples were undertaken at the ITE and UMIST laboratories. Modelling studies of air chemistry and deposition processes have been in progress throughout the period at AERE Harwell and at UMIST.

## 2 ITE-UMIST REPORT

## 2.1 Variations in precipitation and cloud water chemistry with altitude.

Early results of the rainfall composition at Great Dun Fell included in the last report to DoE (April 1985) provided examples of increases in concentration of the major ionic species with altitude, between 350 and 850m. The increases in concentration were generally accompanied by larger rainfall amounts at the summit, so that marked gradients of increasing wet deposition with altitude were observed, much larger than those predicted by the DOE Acid Deposition Review Group (Barrett et al 1983). During the 1985 spring and autumn field campaigns at Great Dun Fell, more extensive (and intensive) measurements of precipitation and cloud water composition were made; publications are in preparation.

During the first three field seasons (autumn 84, and spring and autumn 85) 25 events were recorded with precipitation chemistry measurements at 8 altitudes, 17 of which included cloud water composition. Of these 25, 19 showed an increase in concentrations of the major ions (especially  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  &  $\text{H}^+$ ) with altitude. A further 3 showed concentrations declining with altitude, while the remaining events showed too much scatter in the data to be interpreted as evidence of any systematic effects. For the events in which an increase in concentration with altitude was observed, the increases, expressed as a ratio (concentration at the summit/concentration at the lowest site), were between 1.5 and 6 for all ions. Table 1 summarizes the data for major ions and rainfall amounts.

Measurements at the site generally showed larger concentrations in cloud water than rainwater, increasing on average by a factor between 2 and 4 (Table 2).

Measured concentrations of the major ions in cloud water were largest at cloud base and declined with altitude, generally at rates close to those predicted from the adiabatic lapse rate, although entrainment of dry air into the cap-cloud at the summit of Great Dun Fell was not uncommon, leading to a smaller decline in cloud water ion concentration with altitude. These major features of the precipitation and cloudwater composition were well illustrated by the episodes on 8 November 1985, on which rainfall and cloud water samples were obtained at up to 8 different altitudes on Great Dun Fell. The results of field measurements have also been compared with the results from a model of orographic rainfall enhancement by the seeder-feeder mechanism.

## 2.2 Meteorological situation

On 8 November 1985 there was a generally SW flow with a geostrophic wind speed of about  $15 \text{ ms}^{-1}$ . An occluded front was moving across the area, giving rise to an average rainfall rate of about  $0.6 \text{ mm ha}^{-1}$  in the valley upwind of Great Dun Fell.

Figures 1a-c show the variation in the rainfall rate, the sulphate concentration of the rainfall and the deposition rates of sulphate with altitude. The rainfall rate was obtained by dividing the volume of water collected by the duration of the rainfall as revealed by the raindrop disdrometer (an instrument, which was run continuously at the valley site, for measurements of rain drop size distribution). Figures 1a-c also show the model predictions of the three parameters; these

will be discussed below. It can be seen that the rainfall rate, sulphate concentration and sulphate deposition rate all increased markedly with altitude, as would be expected if rainfall enhancement were occurring by the seeder-feeder mechanism. It is apparent that considerably more scatter from gauge to gauge occurred in the sulphate data than in the rainfall data. This was probably due to selective capture of the larger drops by the rain gauges at high altitude where the winds are strong, because the smaller drops contain the highest sulphate concentrations. The magnitude of the selective capture depends on the exact exposure of an individual gauge.

Figure 2 shows the sulphate concentration in cloud water at the collection sites for the three runs during the later half of the rainfall period. The sulphate concentration decreased with height, the droplets growing larger as the air ascended the hill. The changes in sulphate concentration can be explained entirely by dilution; there was no evidence of any significant sulphate production on this occasion. The sulphate concentrations in cloud water were always considerably in excess of those in rainwater (Table 2).

Figures 3a and 3b show measurements of the cloud liquid water content at the van and summit sites made with Knollenberg forward scattering spectrometer probes. These measurements show that during the early morning an approximately adiabatic increase in liquid water content occurred.

### 2.3 Comparison with a numerical model

The model was based on the model of the seeder-feeder mechanism described by Carruthers and Choulaton (1982), modified to include aerosol scavenging. The sulphate measurements in cloud water were used to characterize the chemical composition of the feeder cloud water, which is a function of the liquid water content and the amount of sulphate scavenged. The structure of the atmosphere and the windspeed data (required as input to the model) were deduced from radiosonde data and cloud base height, obtained by direct observation. The chemical concentration of rain collected in the valley was taken as characteristic of rain which had not passed through the feeder cloud.

The predictions of the model are shown in Figures 1a-c. Comparison with the data shows that, although considerable scatter exists in the data, particularly in the sulphate concentrations, useful predictions of all three parameters have been made.

Very similar results were obtained for nitrate, but the chloride results did not fit the model well. The chloride concentration was greater in rain than cloud at times, a finding which probably reflected the maritime origin of the air in the seeder cloud. Most of the chloride scavenging probably took place above the lowest kilometre of the atmosphere, where the seeder-feeder mechanism is dominant.



### 3 AERE-UMIST REPORT

#### 3.1 Air and cloud chemistry measurements and the field determination of SO<sub>2</sub> oxidation rates.

This section of the report describes progress with the measurements of gas and liquid phase H<sub>2</sub>O<sub>2</sub>, and concentrations of SO<sub>2</sub>, NO<sub>2</sub>, O<sub>3</sub>, hydrocarbons, aerosol SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>. The measurements were made at Great Dun Fell summit (847m), on Silverband mine road (640m), and at Wharley Croft (300m). Examples are provided of key days during the autumn 1985 field campaign when a combination of suitable weather conditions and correctly functioning chemical and meteorological instruments provided field estimates of SO<sub>2</sub> oxidation rates in cloud water.

#### 3.2 Measurements of hydrogen peroxide

Measurements were made by two different techniques, using a Luminol type instrument and a fluorimetric instrument.

##### 3.2.1 Measurements using the Luminol method

The instrument was calibrated using dilutions of stock H<sub>2</sub>O<sub>2</sub> in Analar water. Figure 4 shows that the instrument response over the range 0.25 μM l<sup>-1</sup> to 100 μM l<sup>-1</sup> was nearly linear (slope 1.14). The response of the instrument was consistent, with a coefficient of variation of less than 2% at the 50 μM level for samples analyzed over a period of a few hours. There was some evidence of a drift in response over a longer period, thought to be the result of the ageing of the PVC pump tubes. Variations in the activity of microperoxidase have been observed following periods of storage.

For the working range of 1 to 10  $\mu\text{M l}^{-1}$ , the noise was equivalent to about 6% of the signal. When the  $\text{H}_2\text{O}_2$  concentration was below 1  $\mu\text{M l}^{-1}$ , noise increased, and was of the order of 30% at 0.05  $\mu\text{M l}^{-1}$ . However, if necessary the analyzer could be modified for operation at smaller concentrations.

### 3.2.2 Field measurements, spring and autumn 1985

Cloud water samples were collected on 16 April over the period 1000-1710 GMT and analysed for  $\text{H}_2\text{O}_2$ . Concentrations ranged from 3 to 53  $\mu\text{M l}^{-1}$  (summarized in Figure 5) with marked variations, and the pH of cloud water increased from about 4.8 to 5.4 during the sample period. Sulphate concentrations in cloud water were largest (330  $\mu\text{M l}^{-1}$ ) in the morning and declined to 100  $\mu\text{M l}^{-1}$  by 1600 GMT.

Weather and site difficulties limited further measurements to the period 9-10 May during the spring campaign. During this period,  $\text{H}_2\text{O}_2$  analyzers from Harwell and UMIST were operated in parallel to allow comparison. Both instruments performed well, with very similar responses. As long as care was taken to calibrate both instruments at regular intervals with the same standard solutions, no problems of comparability were encountered.

Care was taken during these measurements to minimize contamination of cloud water samples by dust from the construction work and associated traffic on Great Dun Fell. The results of measurements are summarized in Table 3. During period A the local wind was NW,  $\text{H}_2\text{O}_2$  and  $\text{SO}_4^{2-}$  concentrations were steady, and pH neutral.

For period B, the wind veered to NE and drizzle began,  $\text{H}_2\text{O}_2$  and  $\text{SO}_4^{2-}$  concentrations declined to  $3-5 \mu\text{M l}^{-1}$  and  $20-30 \mu\text{M l}^{-1}$  respectively. The pH of these samples was between 3.0 and 4.3.

On 10 May some samples which had been contaminated by site activity were collected. Results from these samples (see Table 4) showed very small  $\text{H}_2\text{O}_2$  and large  $\text{SO}_4^{2-}$  concentrations; the pH values were between 2.1 and 4.25.

Figure 6 summarizes results from the sampling periods. Air trajectories show that air samples at Great Dun Fell on 16 April had not passed over major UK sources of air pollutants, whereas those for 9 May showed that, even though the wind approached the site from the north, the air came from Eastern Europe, and sooty deposits in cloud water samples were typical of other, similar, episodes with trajectories over E. Europe.

During the autumn campaign the weather was seldom suitable for cloud water sampling (it was either raining, snowing or sunny). However, the samples that were obtained showed very small  $\text{H}_2\text{O}_2$  concentrations (generally less than  $1 \mu\text{M l}^{-1}$ ), much smaller than the spring values, reflecting probably much reduced photochemical production of  $\text{H}_2\text{O}_2$  precursors.

### 3.2.3 Construction of fluorimetric analyzer

During mid 1985, details of a new fluorimetric method for  $\text{H}_2\text{O}_2$  measurement were published (Calvert *et al* 1985). This paper

raised several questions about the Luminol-based analyzer and possible measurement artefacts due to interferences. Although the Luminol method that has been adopted is somewhat different to the one referred to by Calvert et al, it was considered prudent to construct a fluorimetric analyzer to allow further evaluation of the luminescence-based detectors.

The fluorimetric analyzer is based upon the detection of a fluorescent dimer produced following the reaction of  $H_2O_2$  with *parahydroxyphenyl acetic acid* under appropriate pH conditions, maintained by the use of buffer solutions during mixing.

The detection system was built using the spare capacity on the peristaltic pump of a Luminol instrument. This pumping provides the required mixing of reagents, following which the sample including reagents is taken directly into a commercial fluorimeter (Perkin Elmer model LS2B).

The solution is excited at 320nm by a pulsed xenon light source and emission is measured through a 400 nm filter. The fluorescent signal is displayed digitally and taken to a conventional chart recorder.

The fluorimetric system has demonstrated a good linear response over a similar working range to that of the Luminol-based instruments. Some problems have been encountered due to the presence in the reagents of impurities, which, because of their

ability to fluoresce, can elevate the background signal. Steps have been taken to improve the situation, including the use of ultra-pure water and the purification of reagents. It has been found that a pure water supply is important in this respect.

In its present form the fluorimetric analyzer can be operated alongside the Luminol instrument on the same cloud water samples, allowing intercomparisons to be made.

During the autumn campaign, intercomparisons between the Luminol and fluorimetric  $H_2O_2$  analyses were made. The results (Figure 7) show quite large differences between instruments on some occasions but there is no evidence of systematic bias. Further comparisons were made during the spring 1986 campaign, but results of this work have yet to be analyzed.

#### 3.2.4 Gas phase measurements

During a period of no cloud, the fluorimetric  $H_2O_2$  analyzer was modified to give some preliminary measurements of gaseous hydrogen peroxide. The gaseous peroxide was collected by passing sample air through a beaded glass column at  $1.5 \text{ l min}^{-1}$  and mixing this with a stream of Analar water pumped at a rate of  $0.8 \text{ ml min}^{-1}$ . The gaseous peroxide was absorbed in the solution and the aqueous sample pumped into the fluorimetric analyzer.

The system was left to operate for a period of about 36 hours (unfortunately terminated prematurely by a pump failure). The results obtained are summarized in Figure 8.

A measurable signal was produced, from which the values summarized in the figure were derived. Several uncertainties need to be stated concerning the absorption coil. Firstly, although the beaded coil allows efficient absorption of the gaseous  $H_2O_2$ , it is very difficult to establish clearly the residence time in the coil for the absorbing solution. Secondly, the large surface area of glass presented by the beads could well contribute to artefact production of peroxide, as a result of surface reactions of ozone on the glass. The results shown in Figure 8 may represent an elevated baseline resulting from the surface ozone effect, with superimposed peaks corresponding to genuine changes in peroxide concentration.

The absorption system has since been modified to minimize surface effects and is currently being evaluated.

### 3.3 Ozone measurements

Two sites were established for ozone monitoring. At the summit station, an AID560 portable ozone analyzer was run continuously in a Tow-a-Van trailer. The signal from the instrument was both logged on to UMIST equipment and recorded on chart recorder.

The second site was established at Wharley Croft where a Bendix series 8000 instrument was operated continuously and the signals were logged on to UMIST equipment with a chart recorder back-up. Figure 9 shows the concentrations recorded at both sites on 16 November.

### 3.4 Aerosol sampling

Aerosol samples were collected on filter paper on 7, 15 and 16 November. (Figures 10a & b show results of sampling on 16 November). Subsequent analysis of the paper samples for sulphate, nitrate and chloride indicated that the sampling time of 20 mins provided insufficient amounts when clean air was being sampled. In future, the sampling time will be extended to one hour, to give an acceptable signal/background ratio for the paper.

### 3.5 Hydrocarbon results, autumn 1985

Six air samples were collected in stainless steel containers and subsequently analyzed. Two samples were collected on each of the days, 7, 8 and 16 November.

In general, the samples collected on 7 November contained levels of hydrocarbons only marginally elevated when compared with those observed in clean air for the same time of year. The exceptions were the C<sub>6</sub> hydrocarbons 2-methylpentane, 3-methylpentane and n-hexane, which were more significantly elevated. These results were in accord with other measurements suggesting the air was fairly clean (eg the SO<sub>2</sub> levels were very low, being 1 ppbv or less).

The samples collected on 8 November showed some elevation of all the hydrocarbons measured, which suggested the air mass had crossed a small source of general pollution, probably urban. The SO<sub>2</sub> concentration was still low, varying between 1 and 2 ppb.

The samples collected on 16 November were both from the early stages of the sampling period. There were significantly elevated levels of all the hydrocarbons, and SO<sub>2</sub> levels of 4 to 7 ppb. This suggested that the air mass sampled had passed over a fairly large source of pollution. During the afternoon the SO<sub>2</sub> levels declined with a change of wind direction. However, there were no hydrocarbon samples collected that would have confirmed the presence of cleaner air.

### 3.6 SO<sub>2</sub> measurements

Four flame photometric (Meloy) SO<sub>2</sub> analyzers were used for the spring and autumn 1985 campaign. As small differences in SO<sub>2</sub> concentration between the valley sites and the summit were anticipated as part of the experiment, the calibration and zero stability of all instruments received considerable attention and this exercise consumed much of the time during the spring 1985 campaign. During the 9 and 10 May 1985 the instruments provided consistent values, demonstrating that ambient SO<sub>2</sub> concentrations were 1 ppb.

During the autumn more extensive measurements were made, showing very small concentrations (1-2 ppbV SO<sub>2</sub>) on 6, 7 and 8 November but providing useful information about zero stability of the different instruments in the field. The most important data, those for 16 November, are considered in the next section.



### 3.7 Analysis of data for 16 November 1986

Following the autumn campaign, several key days were identified for further analysis. These were the days with suitable meteorological conditions, adequate SO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> concentrations (and no major instrumentation problems).

#### 3.7.1 Meteorological situation

During 16 November 1985 a SW airflow covered the area with a cold front in the Irish Sea moving east. Figure 11 shows a series of air trajectories to the site during the course of the experiment. Two sets of batch samples were collected: run 1 (11.30GMT to 15.15GMT) and run 2 (15.15GMT to 17.30GMT). Between these two runs the cold front passed over the site, marked by a veering in the wind direction, introducing much cleaner air with an oceanic trajectory to the Fell. This was also marked by a drop in windspeed from about 15 ms<sup>-1</sup> to about 8 ms<sup>-1</sup> at the summit.

#### 3.7.2 Results

Figure 12 shows the variation in sulphur dioxide measured at the summit and in the liquid water contents measured at the summit and Silverband sites. Examination of the liquid water content traces shows that dry air entrainment was affecting the clouds strongly near the summit (the adiabatic change between the 2 sites is about 0.35 g m<sup>-3</sup>). This is supported by the ozone trace which showed a higher concentration at the summit than at the upstream site, about 20 ppb at the summit and 10 ppb at Wharley Croft. The concentration at the van site was close to that at the upstream site. Based on occasional measurements of cloud base, the van site

liquid water content was very similar to the adiabatic value. It would seem likely that extra hydrogen peroxide was being introduced by this entrainment.

### 3.7.3 Results of batch cloud water analyses

The cloud water samples collected during runs 1 and 2 were stored under refrigeration and analyzed by ion chromatography. Figure 13 shows the sulphate profiles, which reveal a dilution with height, because the droplets grow as air ascends the hill.

As with other case studies during the Autumn period, normalisation shows that no detectable sulphate production was occurring. In this case there was no evidence of any relative increase in ammonium ions with height.

During run 1 it was apparent that the sulphate concentration at the summit was considerably lower than at the van site despite the liquid water contents being almost equal. Table 5 summarizes the time histories of droplet number concentration and mean radius at the two sites. Referring to run 1 and emphasizing that data were available at the summit site from 1415GMT, the data show that an increase in the mean radius occurred, diluting the sulphate. However, a reduction in the droplet concentration, due to evaporation following dry air entrainment, also occurred. This reduction in droplet number concentration accounts for most of the reduction in liquid water content below the adiabatic value. The droplets that had been completely evaporated in this

way were converted back to unactivated nuclei. These small aerosol particles were not collected by the cloud water collectors; a similar effect was found during other case studies and is discussed in recent papers on cloud microphysics (Choulaton et al (1986) and Hill and Choulaton (1985)). During run 2, liquid water content was lower at the van site than at the summit, so the same arguments did not apply.

During both runs, most of the chloride in the samples came from sea salt; in both cases the ratio of sodium to chloride ions was close to the sea salt ratio of 0.85 by mass.

#### 3.7.4 Interpretation of the hydrogen peroxide profiles

Figures 14a & b show the hydrogen peroxide profiles for runs 1 and 2. In run 1, the concentration of hydrogen peroxide decreased between the van site and the summit. About 6 ppbv of SO<sub>2</sub> was measured in the gas phase at the same time.

During run 2, however, the SO<sub>2</sub> levels were much lower (close to zero) particularly during the later part of the run and, in the absence of any significant reaction with SO<sub>2</sub>, the aqueous phase hydrogen peroxide concentration increased markedly towards the summit of the hill. This was probably due to dry air entrainment close to the summit, introducing extra hydrogen peroxide. The interpretation of run 2 is confused somewhat by the tendency of cloud base to rise during the experiment. In order to quantify these interpretations, the results were compared with the model predictions.

### 3.7.5 Hydrogen peroxide measurements

The measurements were complicated by variations in the level of cloud base and by entrainment of dry air from above into the cap cloud at the summit, causing marked fluctuations in  $H_2O_2$  (Figure 15). However, there do appear to be differences in the total amounts of aqueous  $H_2O_2$   $m^{-3}$  between the sites, indicating a loss of 0.01 ppbv  $H_2O_2$ . If all of the  $H_2O_2$  loss was due to reaction with  $SO_2$ , the expected  $SO_2$  loss (neglecting the effects of dry air entrainment at the summit) would be  $0.6 \text{ ppbv h}^{-1}$ .

The  $SO_2$  concentration observed at the summit at 1500 GMT was 6 ppbv, suggesting an oxidation rate of the order  $10\% \text{ h}^{-1}$  on this autumn/winter day.

### 3.8 Comparison with the model

The results have been compared with the model of Hill, Choularton and Penkett (1986). The model was run with the following input parameters for run 1 : cloud base 340m above the valley floor; 5 ppbv  $SO_2$ ; 30 ppbv  $O_3$ ; 2 pptv  $H_2O_2$  entering cloud base. The vertical structure of the atmosphere was estimated from radiosonde data from Aughton, Longkesh and Shanwell stations. The model was run with a variable entrainment rate into the cloud which increased with height and was adjusted to reproduce the observed liquid water content. No measurements were available of gas phase hydrogen peroxide entering the cloud from above; the model was therefore run with several different assumed values. Figure 14a shows a comparison between the data and the model predictions for hydrogen peroxide in the entrained air.

For run 2, cloud base was set at 440m. The input gas concentrations were: 0 ppbv SO<sub>2</sub>, 30 ppbv O<sub>3</sub> and 2 pptv H<sub>2</sub>O<sub>2</sub> entering cloud base. The model was run as described above and the effect of varying cloud base was investigated. Comparison of the model and experimental data is presented in Figure 14b, with 6 pptv H<sub>2</sub>O<sub>2</sub> in the entrained air.

In each case the level of agreement between model predictions and the observations supports the suggestion that throughout this case study dry air entrainment introduced extra hydrogen peroxide and that, when present, SO<sub>2</sub> consumed the oxidant at about the rate suggested by the model. It should be noted that the agreement between the model predictions and the data is poor close to cloud base. This is because the model takes one value for cloud base and the H<sub>2</sub>O<sub>2</sub> concentration decreases rapidly with height in the lowest 100 m as a result of dilution. In real cloud, the base level varies by several tens of metres on time scales of seconds to minutes, because of variations in the airstream properties (see Choularton *et al* 1986). Hence the batch samples (which are long term averages) do not show the high concentrations expected very close to cloud base.

### 3.9 Conclusions

The three case studies have shown that, when significant concentrations of sulphur dioxide are present in the airstream, hydrogen peroxide dissolved in the cloud water is consumed at a rate consistent with that predicted by the model of Hill, Choularton and

Penkett (1986). The field reaction rate constant is

$$K_{\text{H}_2\text{O}_2} = 10^6 \text{ mol}^{-1} \text{ s}^{-1}.$$

When the cloud is affected by dry air entrainment from aloft, extra hydrogen peroxide is introduced. The results suggest that the concentration of hydrogen peroxide in the free tropospheric air entrained may be several times greater than in the boundary layer air in which the cloud forms. The reaction rate data suggest that the  $\text{H}_2\text{O}_2$ - $\text{SO}_2$  reaction is fast and is likely to be oxidant limited. Consequently, in many conditions, when oxidation by  $\text{H}_2\text{O}_2$  is dominant over ozone due to low cloud water pH, the rate of sulphate production may be controlled by the rate at which hydrogen peroxide can be entrained into a cloud system.

In these experiments carried out in November, no significant sulphate production was observed. This was expected with the very low hydrogen peroxide concentrations recorded (typically around 5 pptv). However, during the spring months, hydrogen peroxide concentrations around 100 times greater than this have been observed using the same instrumentation. This work will be reported shortly.

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MEAN RATIO OF RAINFALL CONCENTRATION AT SUMMIT/VALLEY, AND RATIO OF RAIN  
 AMOUNT FOR 20 PRECIPITATION EVENTS AT G.D.F. 1984-85, WITH MEASUREMENTS  
 AT 8 LEVELS (244-847 m)

RATIO OF MEAN CONCENTRATION AT SUMMIT/VALLEY FOR MAJOR IONS

H+	NH <sub>4</sub>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	RAIN
2.9	3.1	2.9	2.3	2.2	2.0



TABLE 2

MEAN RATIO OF ION CONCENTRATION OF CLOUDWATER/  
RAINWATER FOR 11 PRECIPITATION AND CLOUDWATER  
EPISODES MEASURED AT GREAT DUN FELL SUMMIT  
DURING 1985.

	$H^+$	$NH_4^+$	$Cl^-$	$NO_3^-$	$SO_4^{2-}$
$\bar{x}$	3.9	2.4	2.6	2.8	2.0

TABLE 3

## CLOUDWATER SAMPLES GDF 9/5/85

GMT	$\mu\text{M}$ $\text{H}_2\text{O}_2$	$\mu\text{M}$ $\text{SO}_4^{2-}$	pH	NOTES	
<u>PERIOD A</u> WIND NORTH WESTERLY CLOUD BASE - 2000 Ft (Mine Road)					
0900	6.5	459	6.90	Overnight sample	
0910	16.0	125	6.97		
0920	15.0	113	6.71		
0932	11.0	124	6.51		
0940	12.5	124	6.80		
0953	13.0	124	6.51		
1003	12.0	149	6.79		
1015	11.0	271	6.76		
<u>PERIOD B</u> WIND NORTH EASTERLY. CLOUDBASE - MINE ROAD. DRIZZLE					
1924	5.0	324	-		Gauge exposed in all these samples
1934	5.0	25.9	4.24		
1941	4.4	26.9	4.30		
1947	3.4	26.6	4.14		
1954	3.5	27.3	4.04		
2002	3.8	28.9	3.71		
2008	3.6	27.5	3.75		
2013	4.3	26.9	3.85		
2020	4.0	26.5	3.64		
2026	4.2	25.0	3.75		
2032		23.1	3.09		
2039		26.5	3.54		
2045		25.1	3.51		
2052		20.5	3.44		
2100		21.0	3.76)		
2110		24.2	3.31)		
2120		25.9	3.29)		

TABLE 4

## CLOUD WATER SAMPLES 10.5.85

WIND DIRECTLY ACROSS SITE (HEAVY VEHICLES) RAIN AND DRIZZLE

	TIME GMT	$\mu\text{M}$ $\text{H}_2\text{O}_2$	$\mu\text{M}$ $\text{SO}_4^{2-}$	pH	NOTES
47	0715	1.0	266	3.80	All samples extremely dirty
48	0730	-	209	3.84	
49	0747	0.6	247	3.94	(sooty deposits)
50	0805	0.7	247	4.25	
51	0824	2.3	298	4.00	
52	0845	4.1	265	2.77	
53	0852	4.8	256	2.62	
54	0905	4.2	252	2.52	
55	0915	5.2	242	2.66	
56	0936	6.0	279	2.94	
57	1000	-	-	2.18	

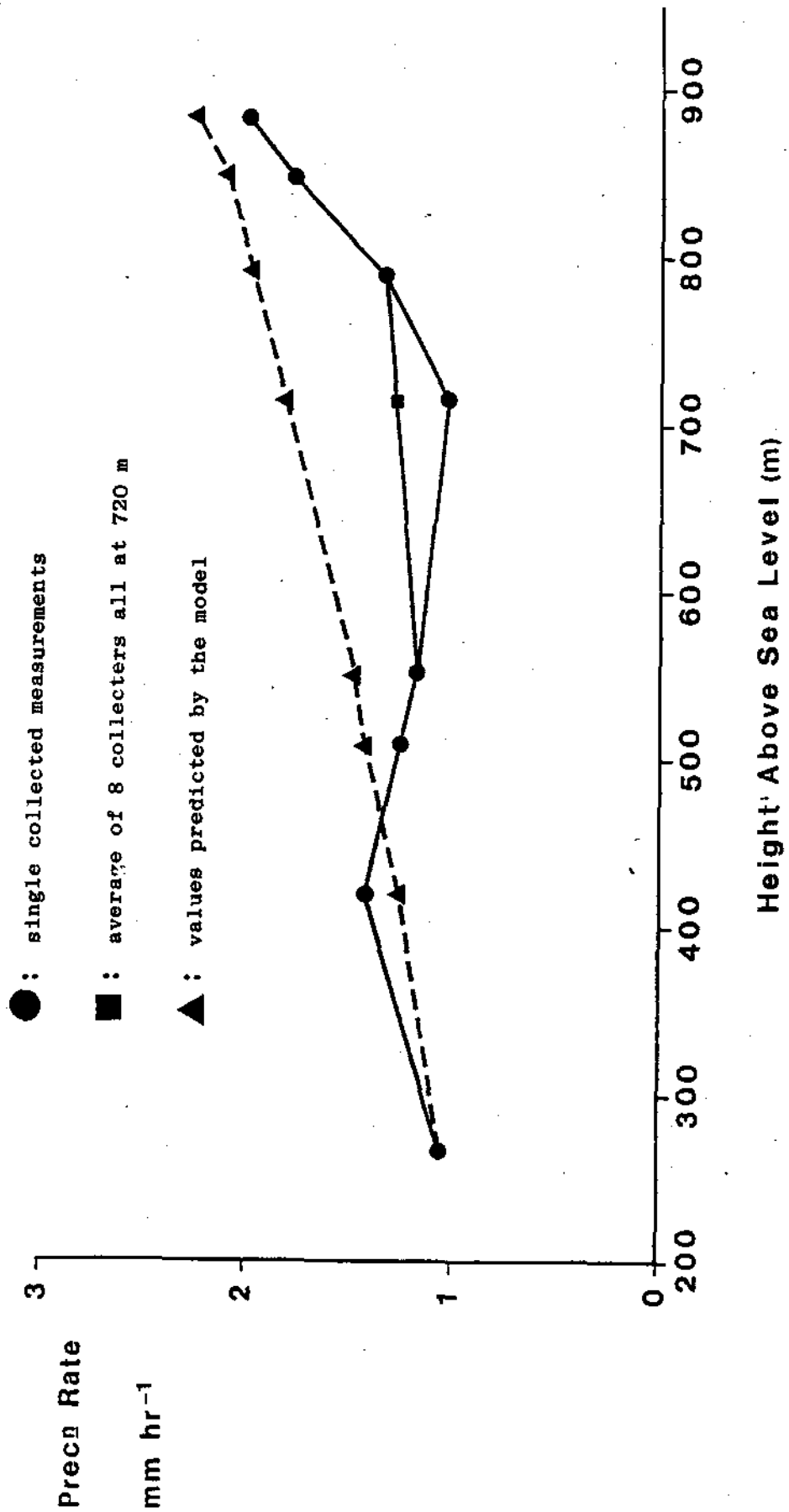
TABLE 5

The cloud liquid water content,  $L \text{ g m}^{-3}$ , droplet mean radius,  $R \text{ }\mu\text{m}$ , and droplet number concentration,  $N \text{ cm}^{-3}$ , measured at the summit and van sites on 16 November 1985.

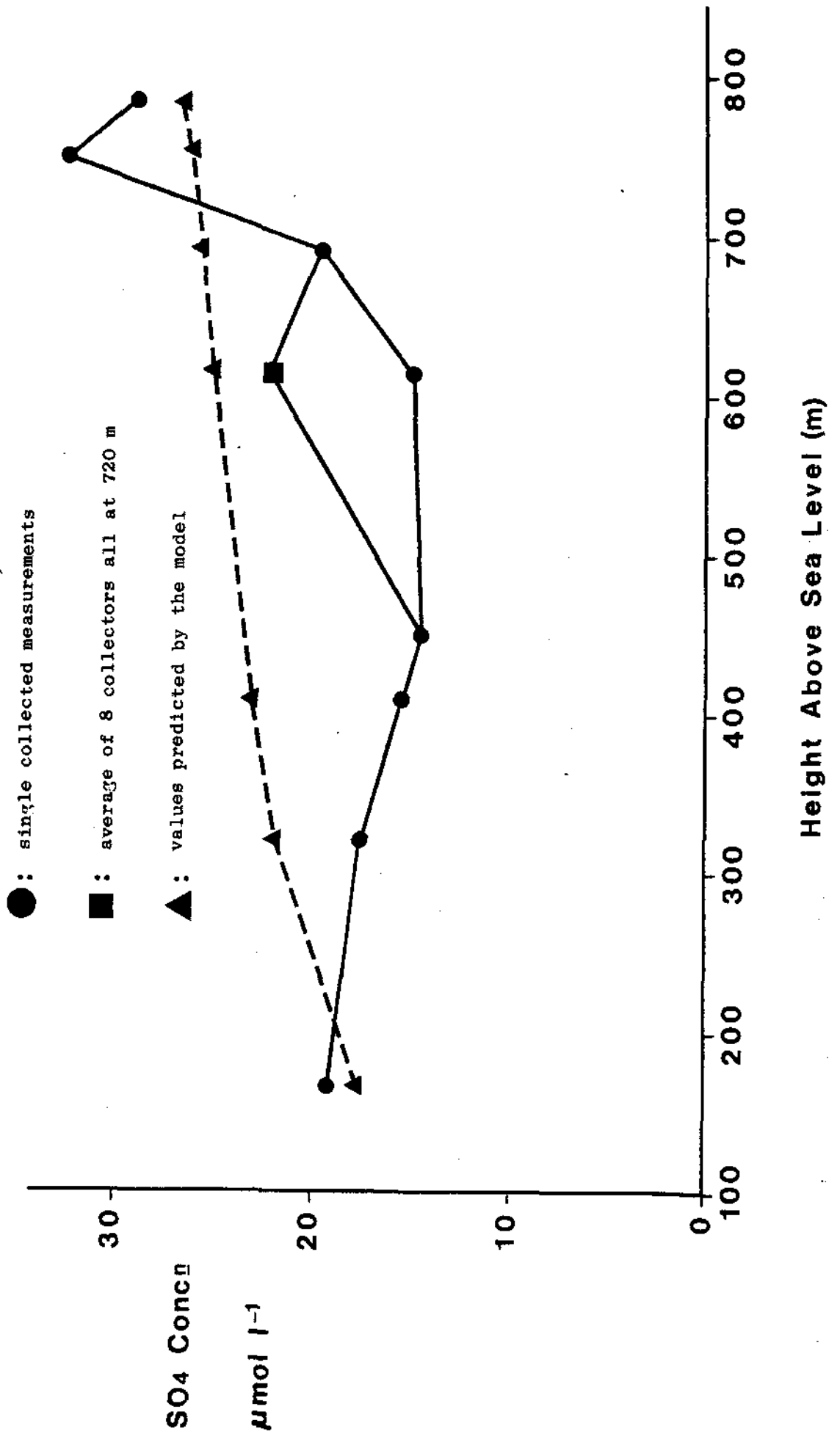
TIME	VAN SITE			SUMMIT SITE		
	L	N	R	L	N	R
14.30	0.32	310	6.2	0.27	250	6.5
15.00	0.40	270	6.5	0.36	170	7.0
15.30	0.18	160	5.0	0.27	120	6.6

FIGURE 1a

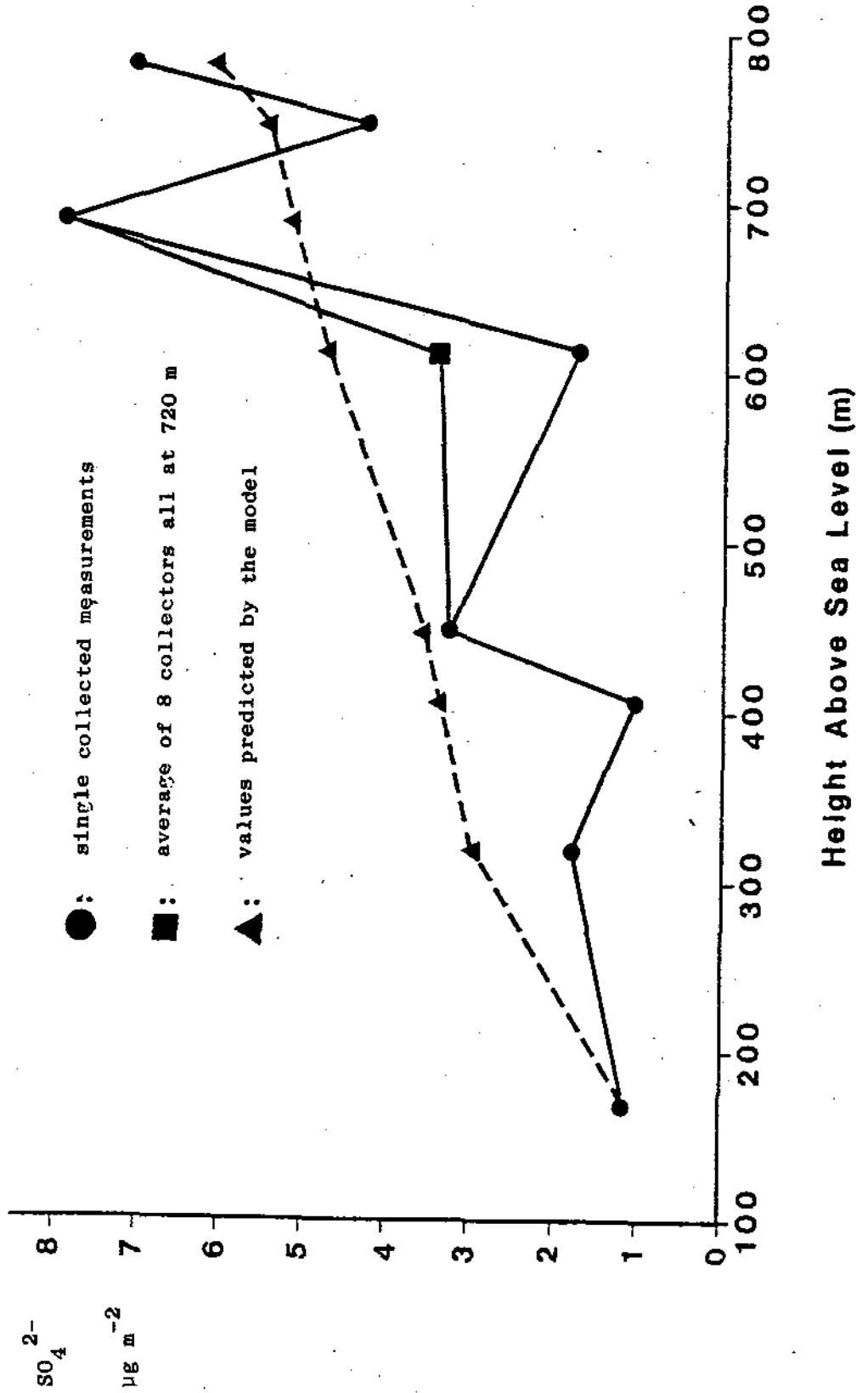
### Precipitation Rate



### Sulphate Concentration in Rainwater



Sulphate Deposition Rate



[SO<sub>2</sub>] profiles for 8/11/85.

+ RUN 1  
○ RUN 2  
□ RUN 3

FIGURE 2

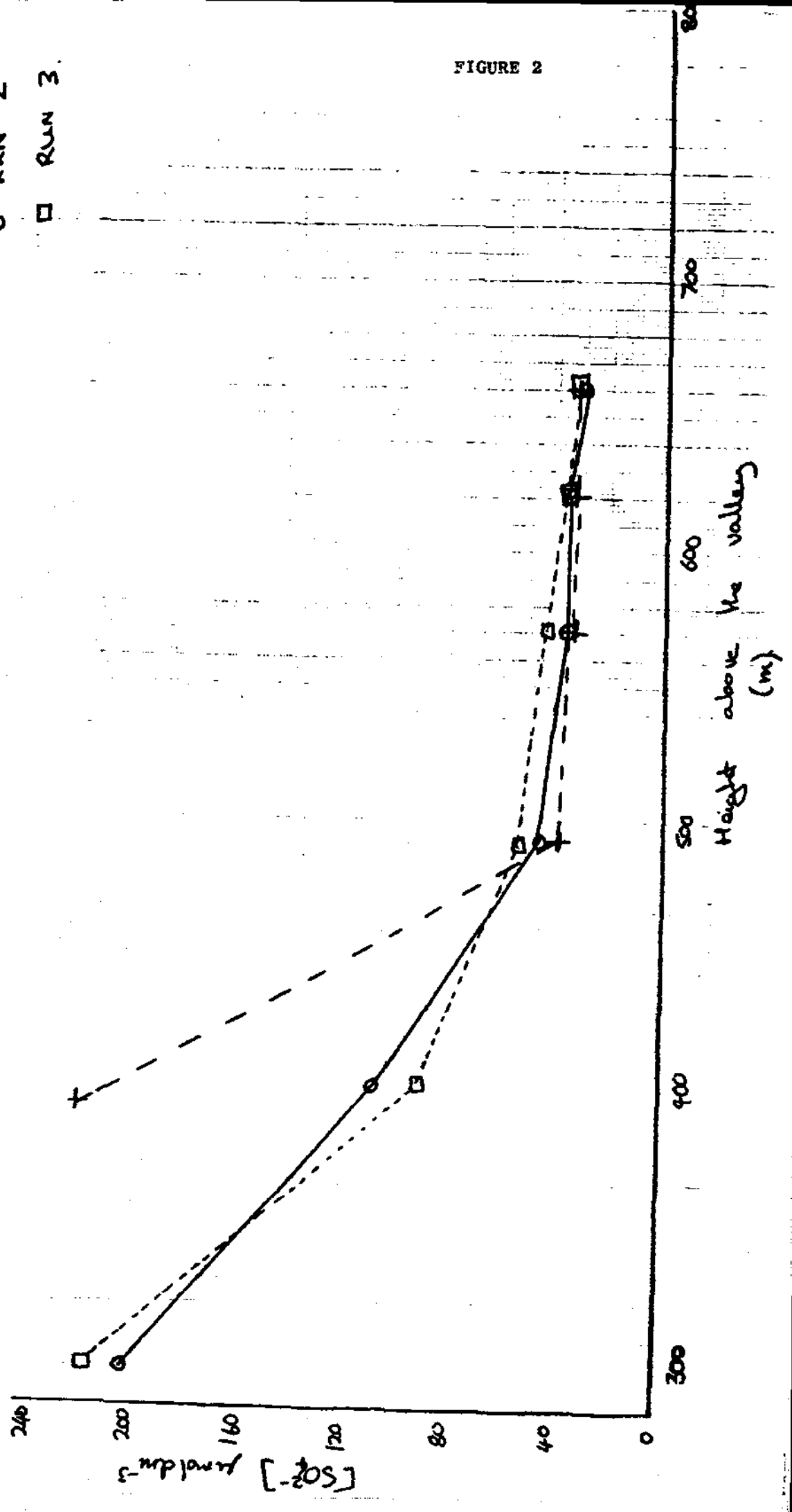




FIGURE 3a

Cloud liquid water content measurements at 720 m on 8/11/1985

MERC Silverband 8/11/85

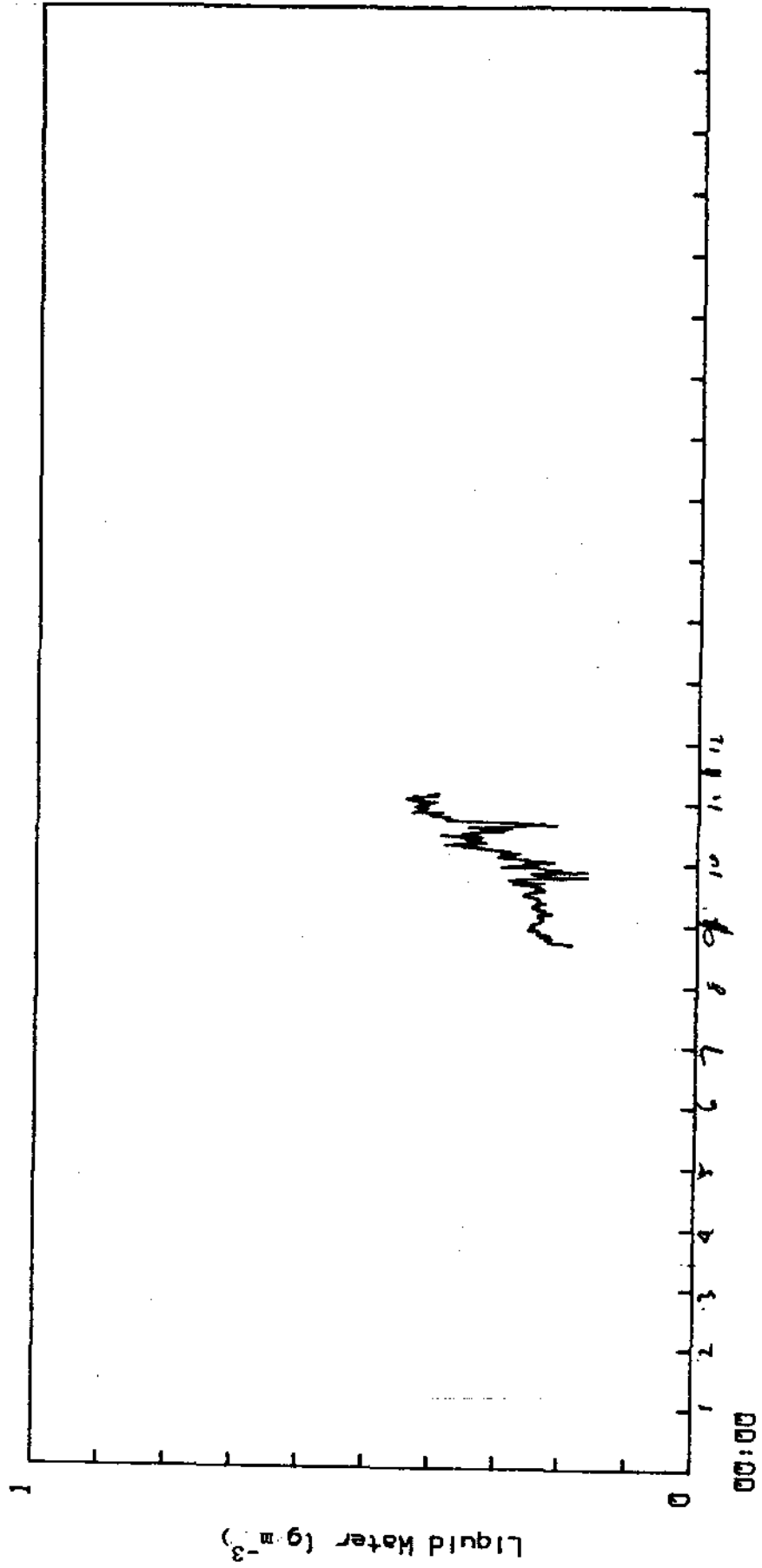
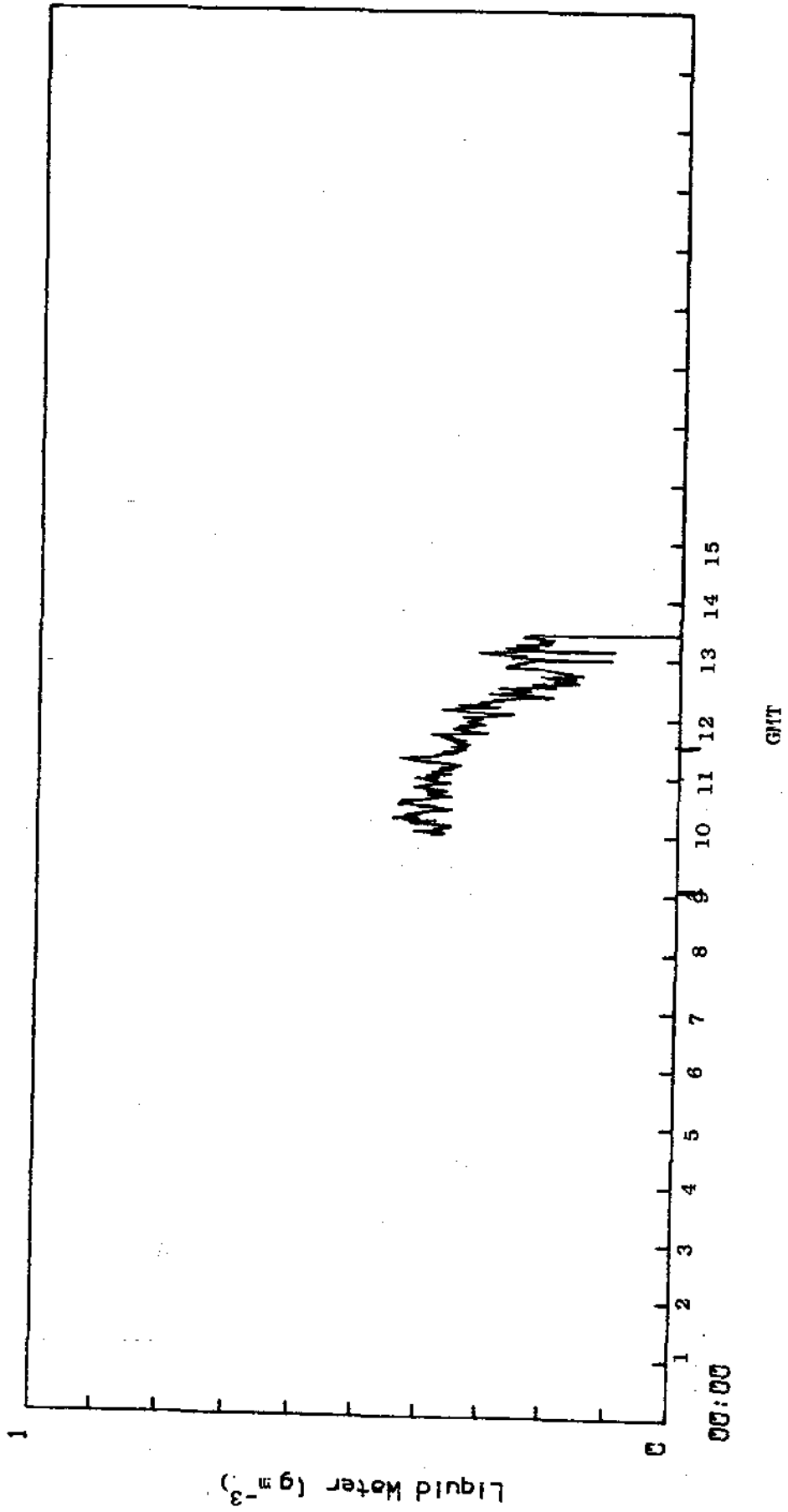


FIGURE 3b

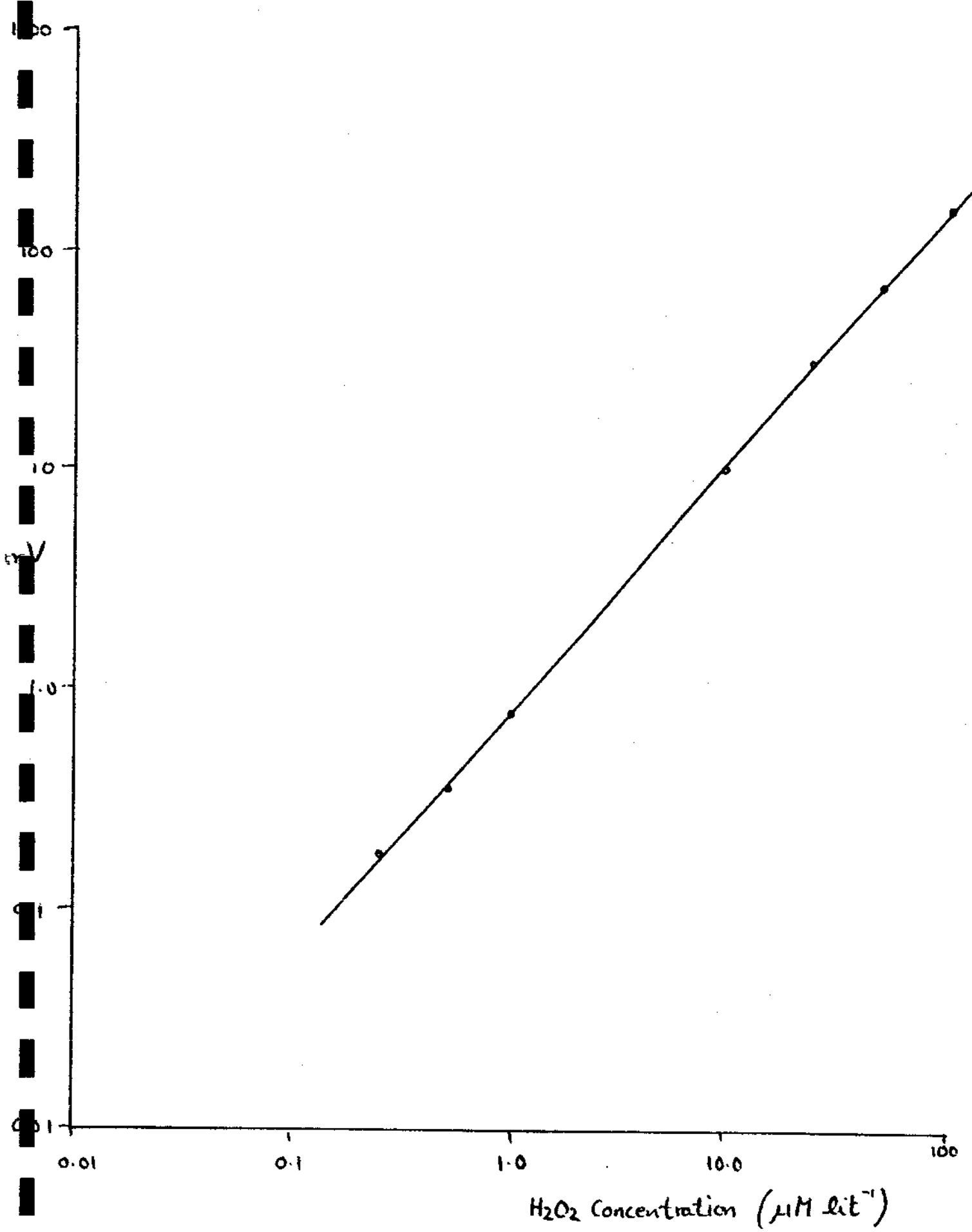
Cloud liquid water content measurements at 847 m on 8/11/1985

Great Dun Fell Summit 8/11/85



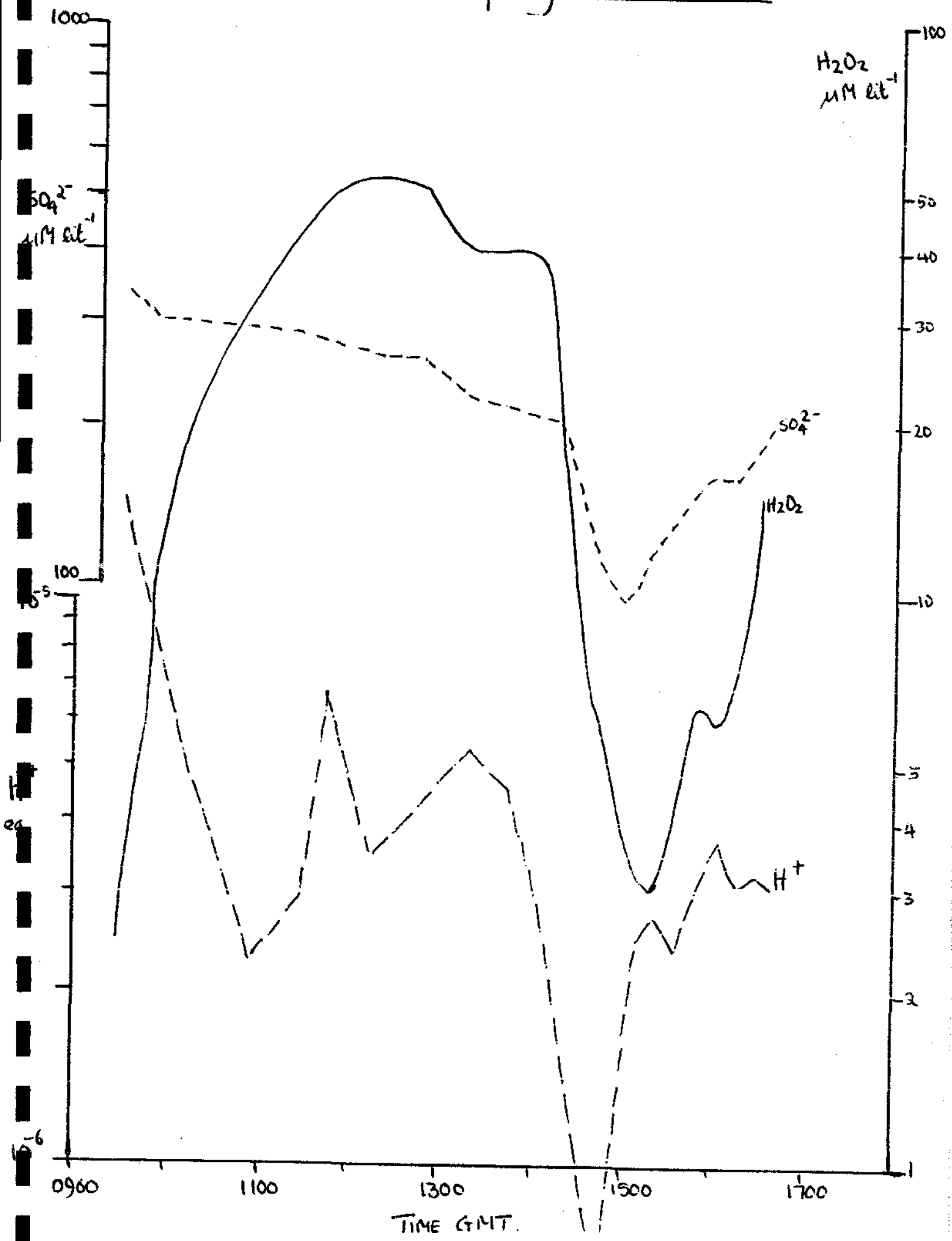
Response of chemiluminescent  $H_2O_2$  analyser

FIGURE 4



H<sub>2</sub>O<sub>2</sub>, H<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> at  
GDF summit Spring 1985, Cloudwater

FIGURE 5

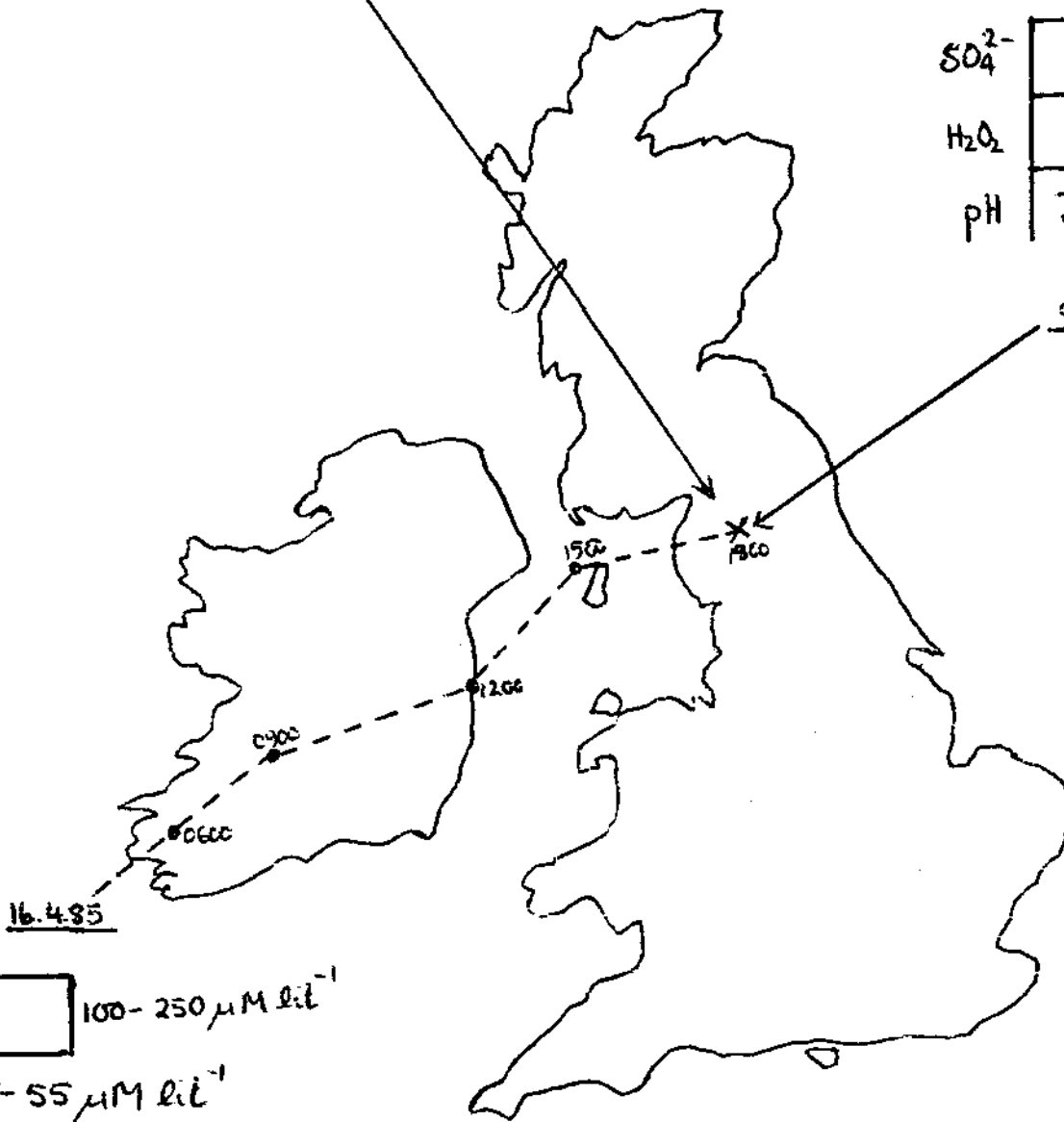


Cloudwater chemistry for clouds arriving at GDF summit  
in air from 3 source regions, Spring 1985.

FIGURE 6

$\text{SO}_4^{2-}$  100-150  $\mu\text{M lit}^{-1}$   
 $\text{H}_2\text{O}_2$  10-15  $\mu\text{M lit}^{-1}$   
 pH 6.5-7.0  
9.5.85

$\text{SO}_4^{2-}$  20-30  $\mu\text{M lit}^{-1}$   
 $\text{H}_2\text{O}_2$  3-5  $\mu\text{M lit}^{-1}$   
 pH 3-5.0  
9.5.85



$\text{SO}_4^{2-}$  100-250  $\mu\text{M lit}^{-1}$   
 $\text{H}_2\text{O}_2$  3-55  $\mu\text{M lit}^{-1}$   
 pH 5-6.0

Comparison of H<sub>2</sub>O<sub>2</sub> analysers.

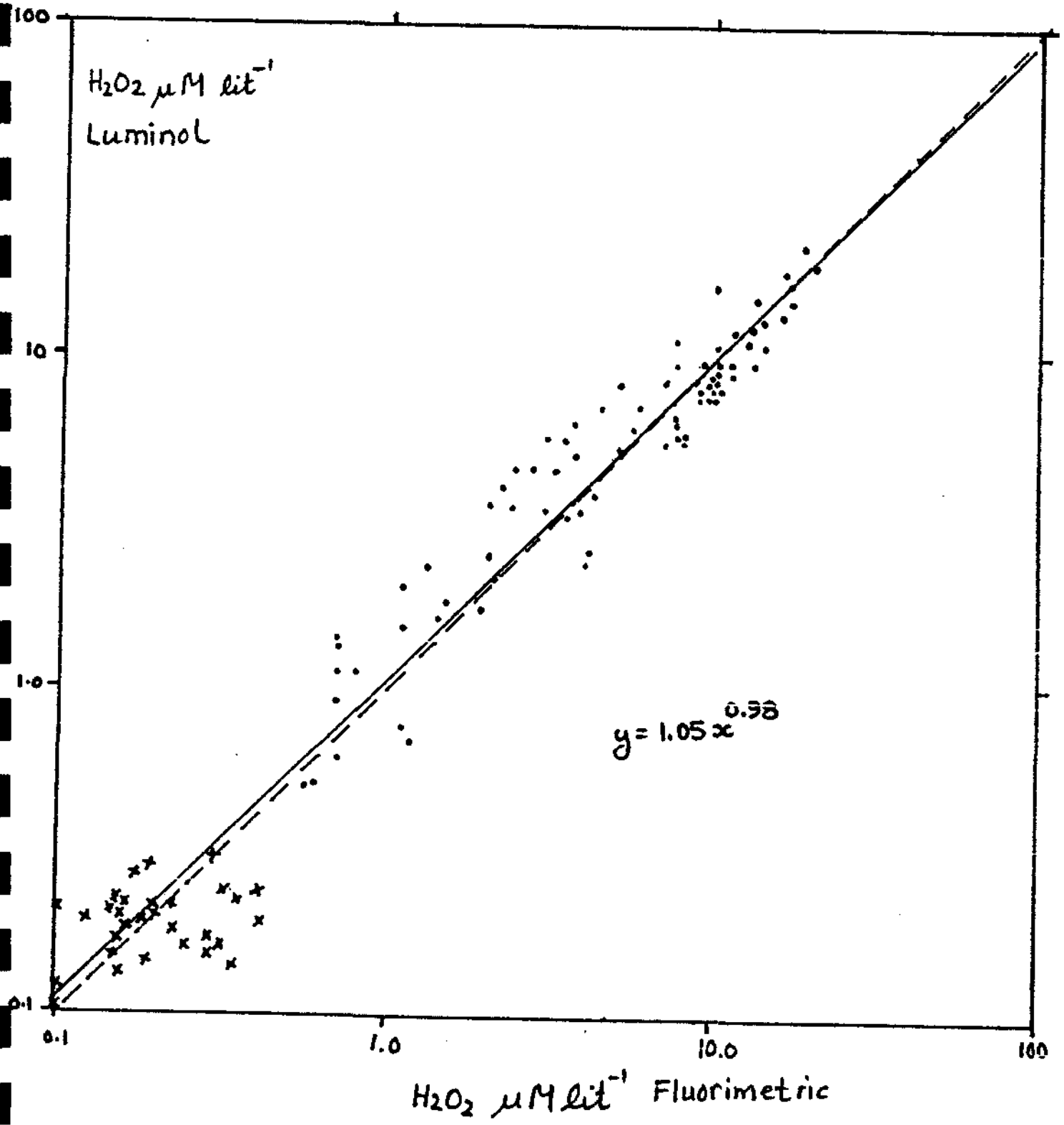


FIGURE 8

Gaseous  $H_2O_2$  measured at GDF summit Autumn 1985 using the  
fluorimetric  $H_2O_2$  analyser

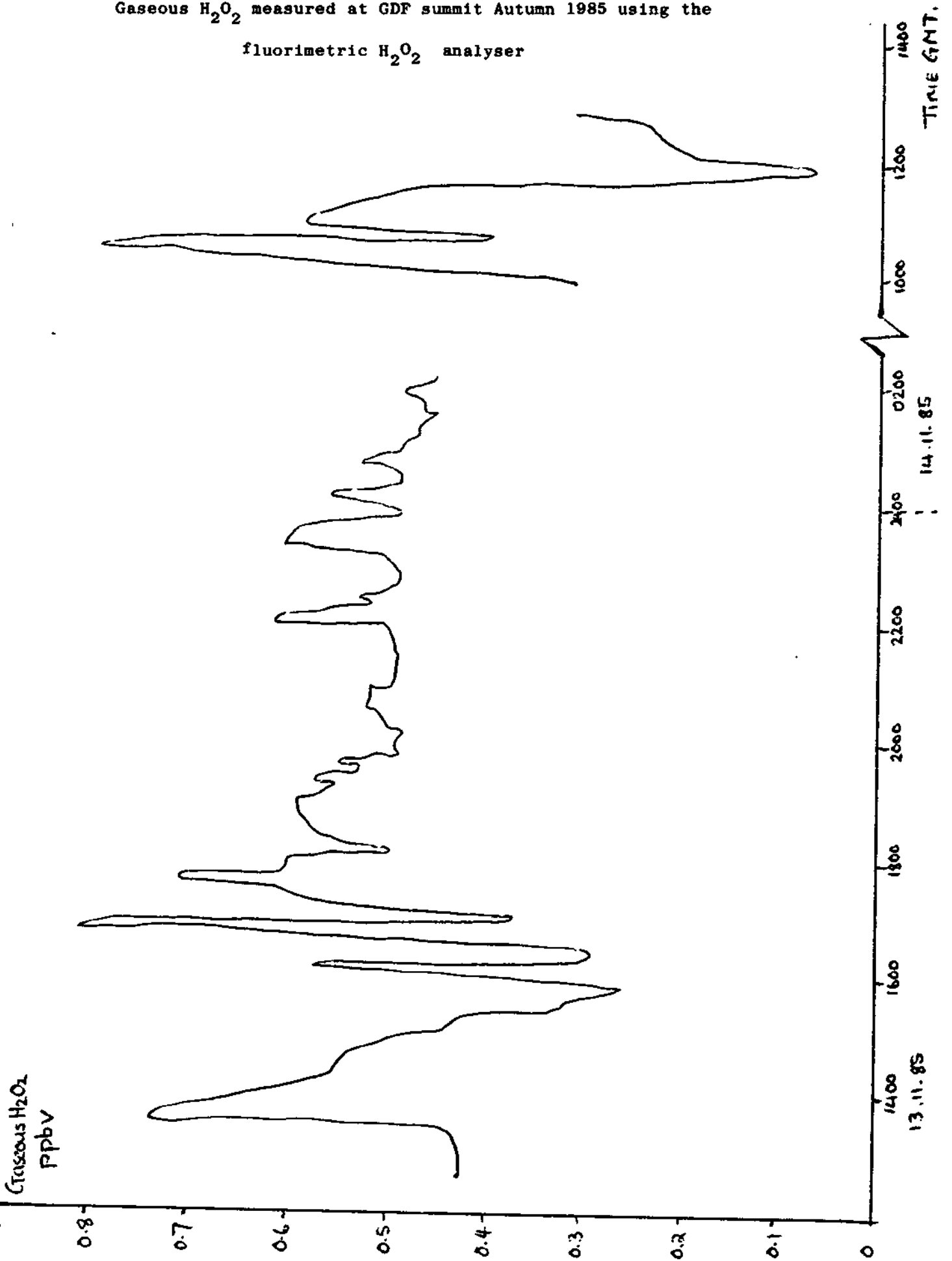


FIGURE 9

Ozone concentrations recorded at GDF summit and Wharley Croft

16 November 1985

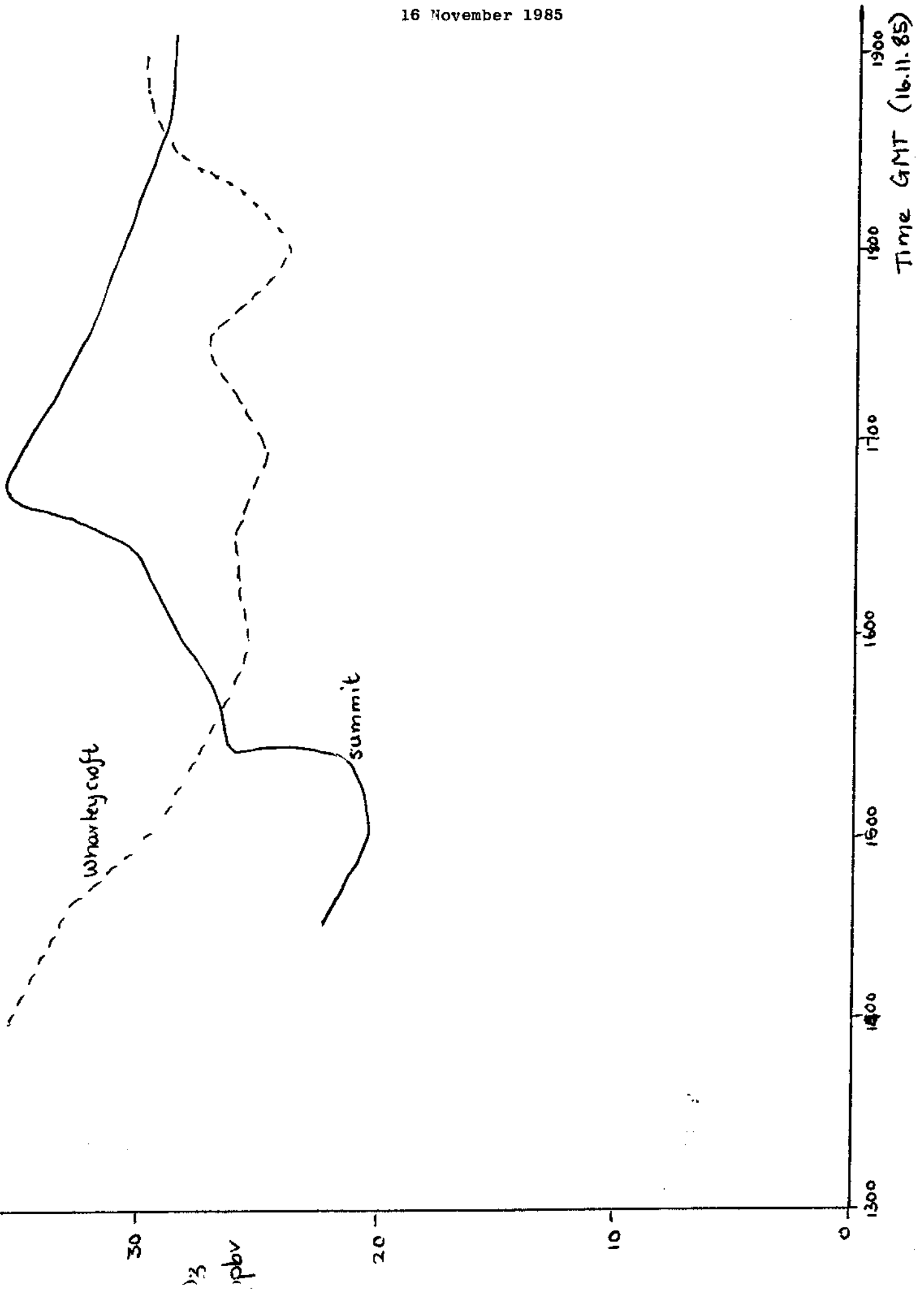




FIGURE 10a

Sulphate aerosol at Wharley Croft, 20 minute sampling period  
16 November 1985

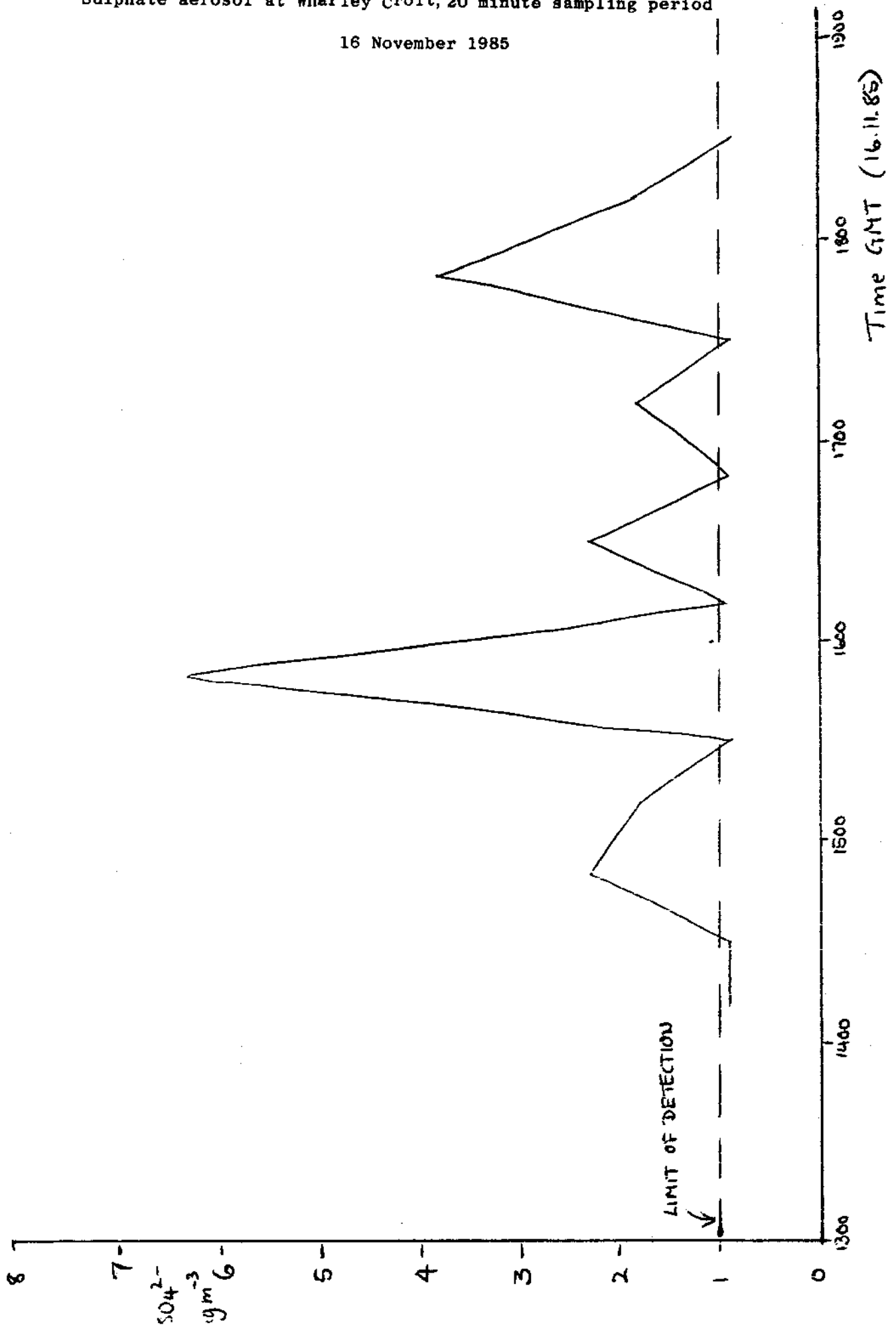
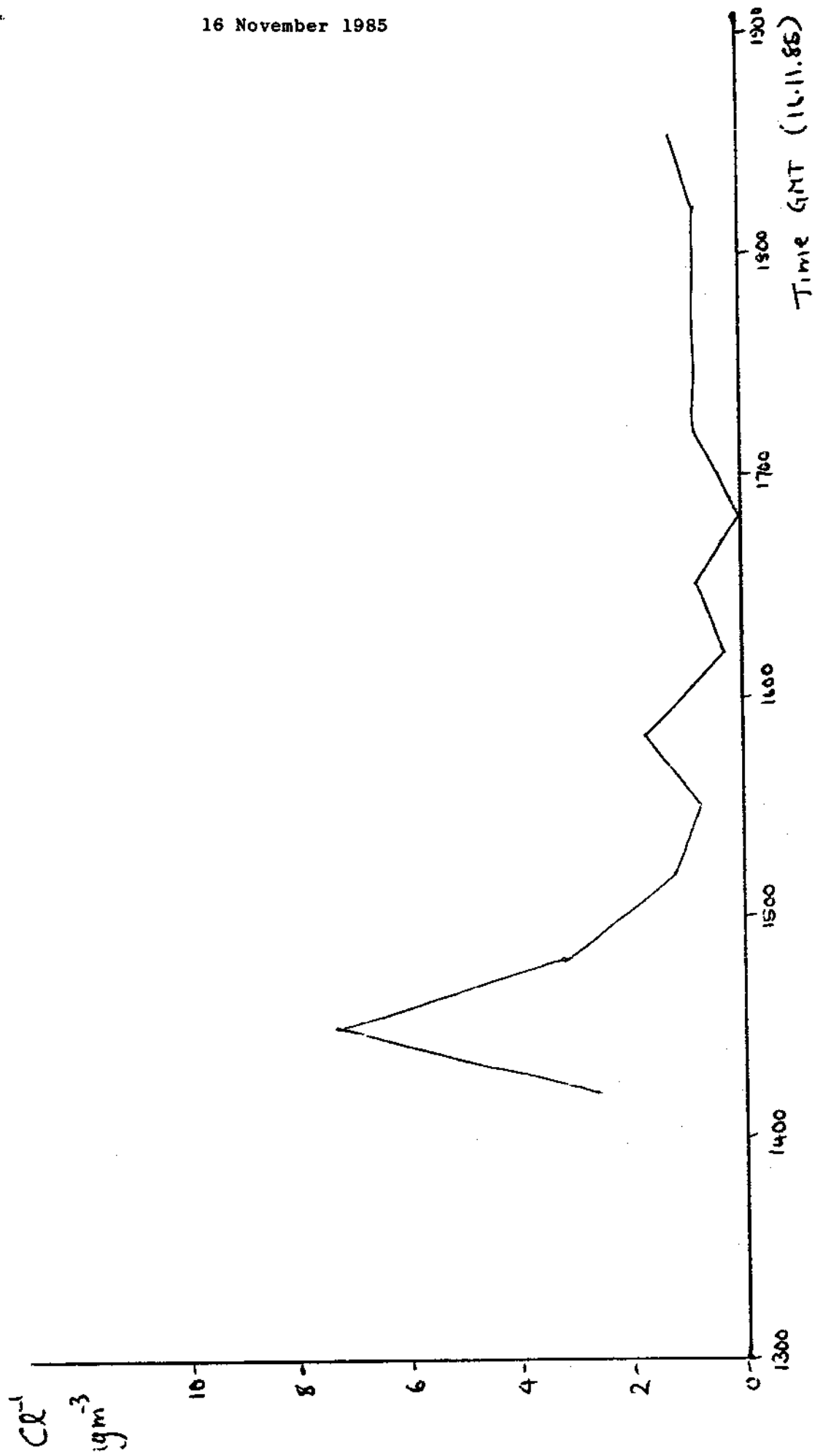


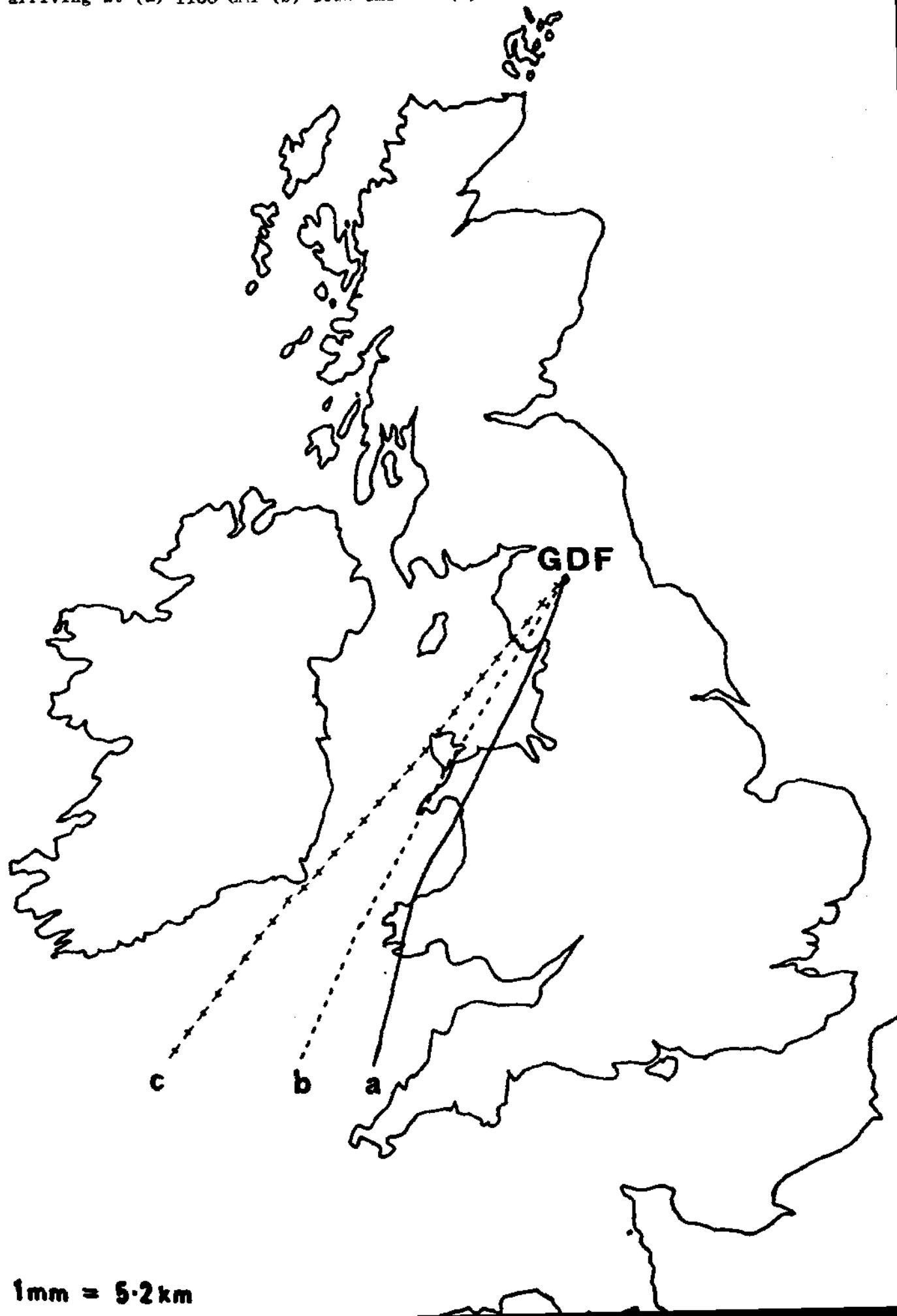
FIGURE 10b

Chloride aerosol at Wharley Croft, 20 minute sampling period,

16 November 1985



Air trajectories to Great Dun Fell for 16 November 1985  
arriving at (a) 1100 GMT (b) 1300 GMT and (c) 1600 GMT



1mm = 5.2 km

FIGURE 12

The variation with time of sulphur dioxide concentration in ppbv (a) at the summit, liquid water content,  $L g m^{-3}$ , at the summit (curve b), and at the van site (curve c) for 16 November 1985.

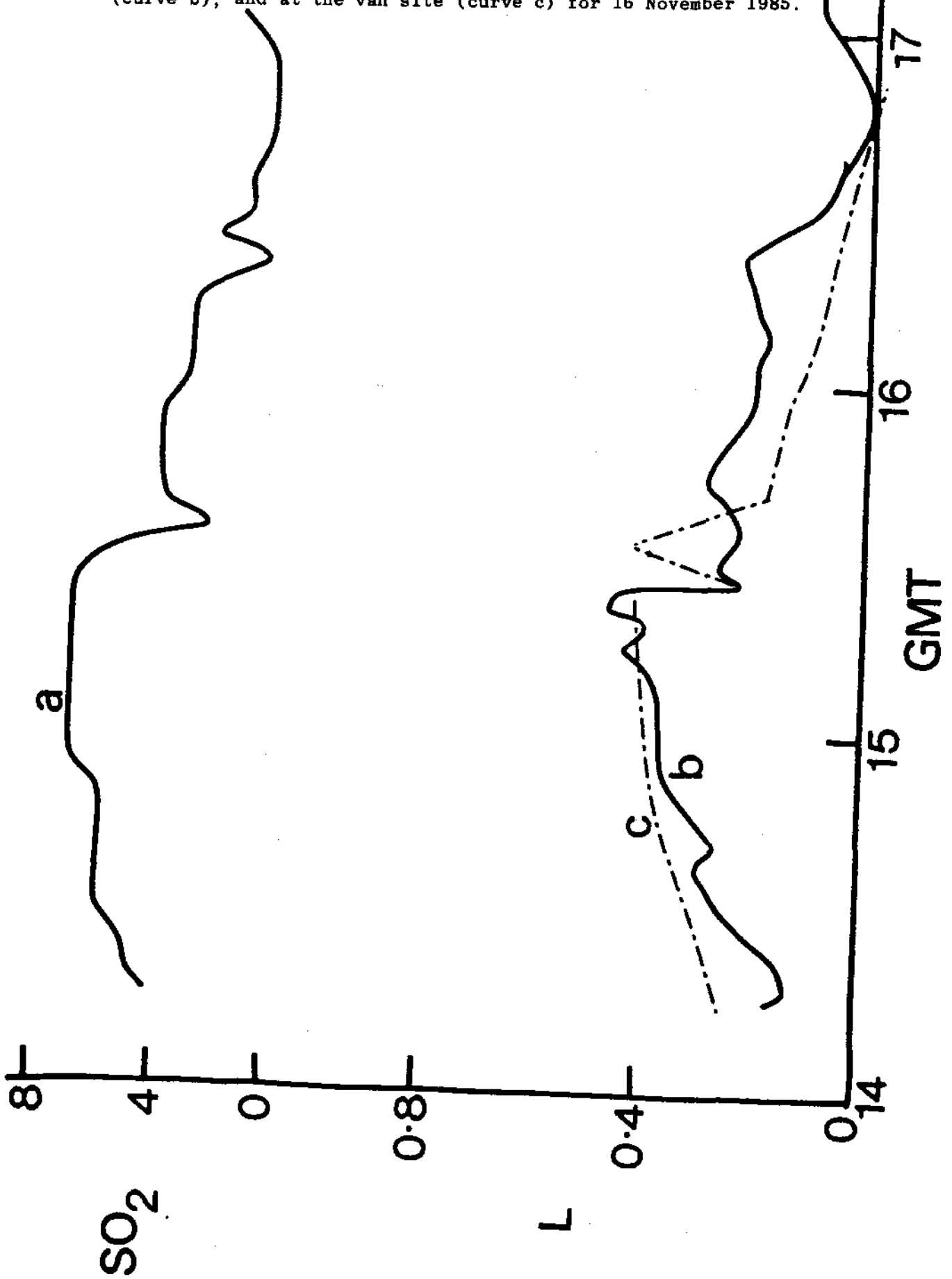


FIGURE 13

The variation of sulphate concentration with height above the Eden Valley, Z, for run 1 (curve a) and run 2 (curve b) on 16 November 1985.

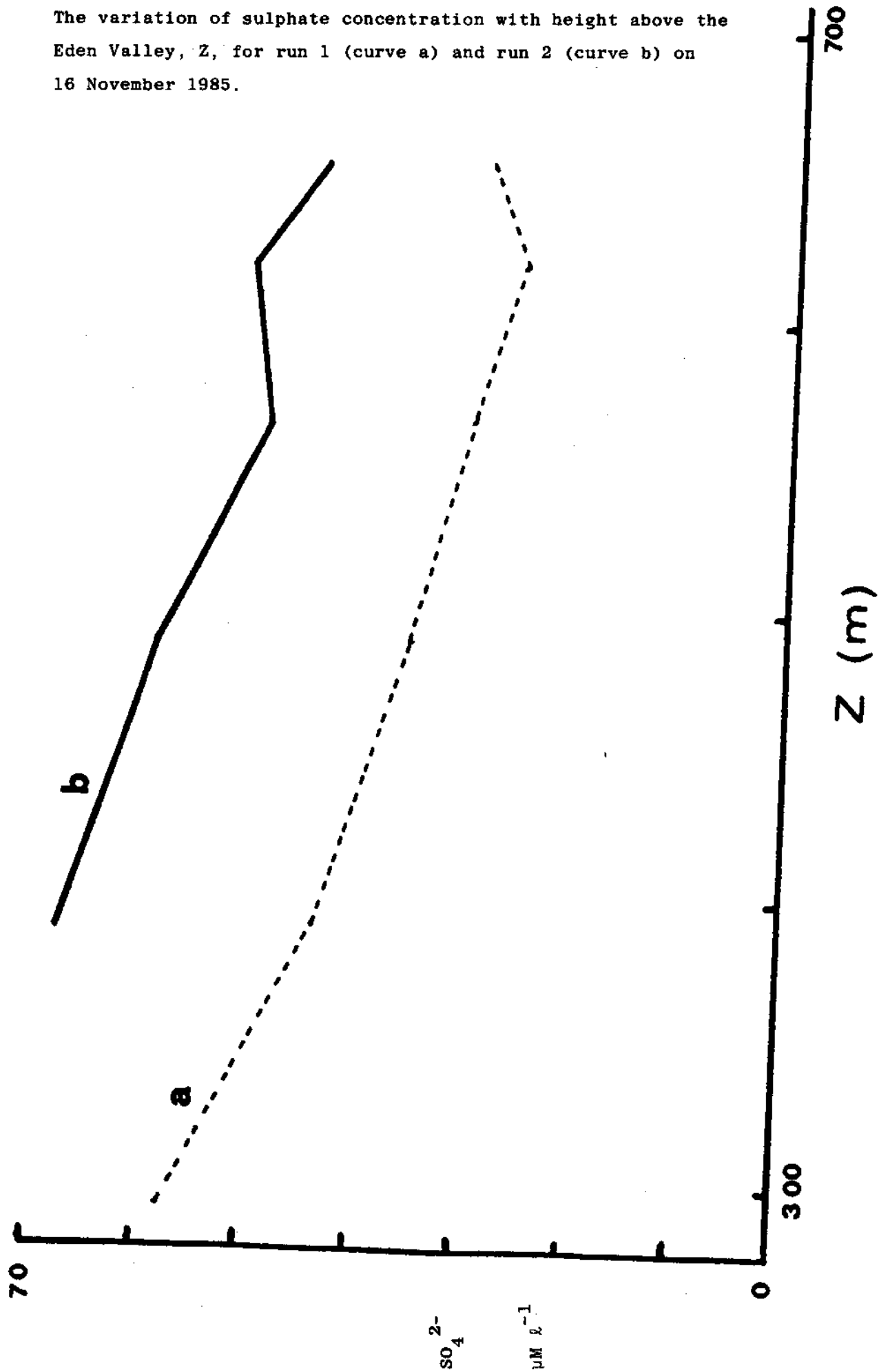


FIGURE 14a

Comparison of the observed (a) and predicted (b) hydrogen peroxide concentrations in batch samples of cloud water, against height  $h$  above the Eden valley for 16 November 1985 (run 1)

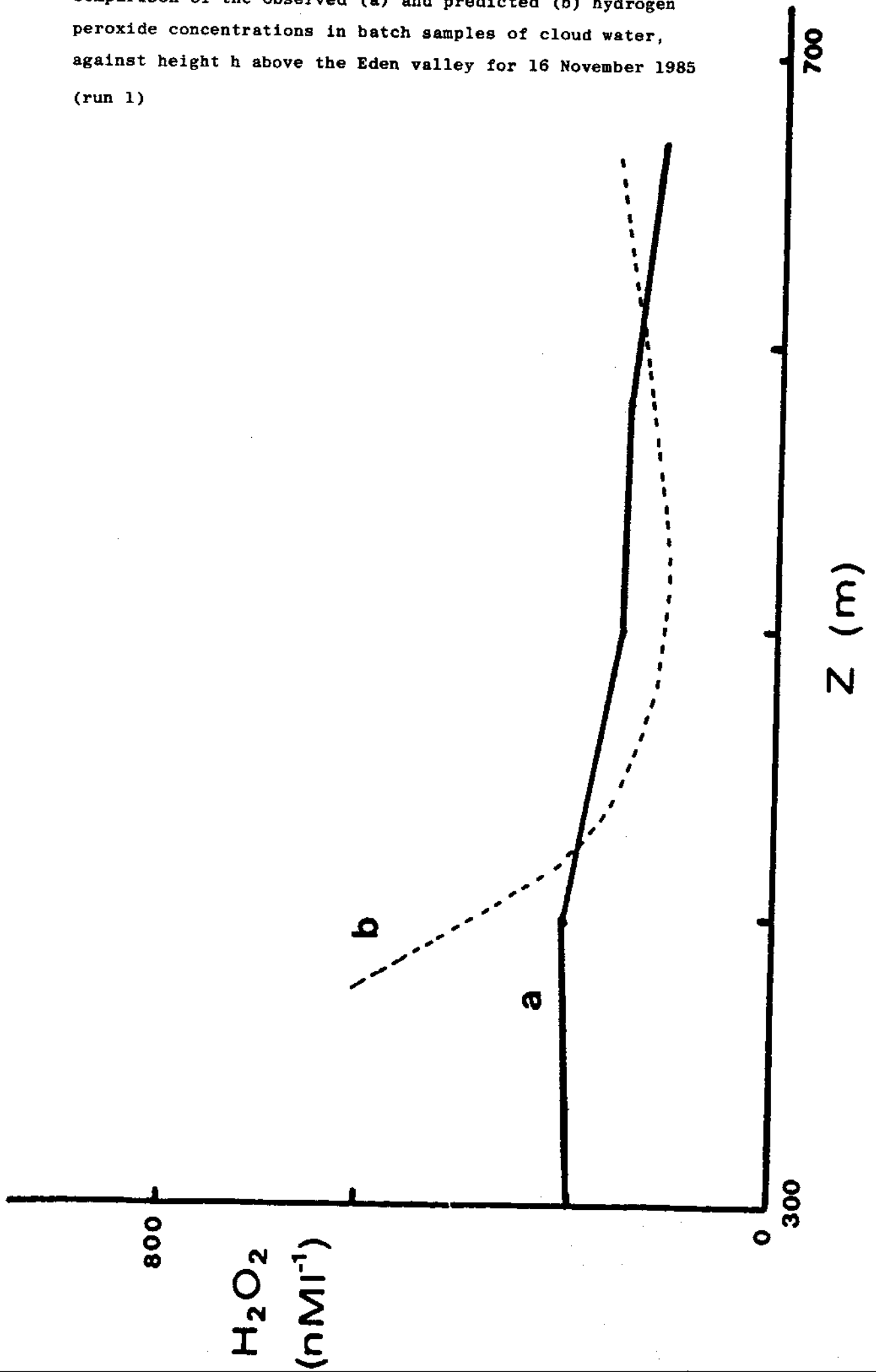
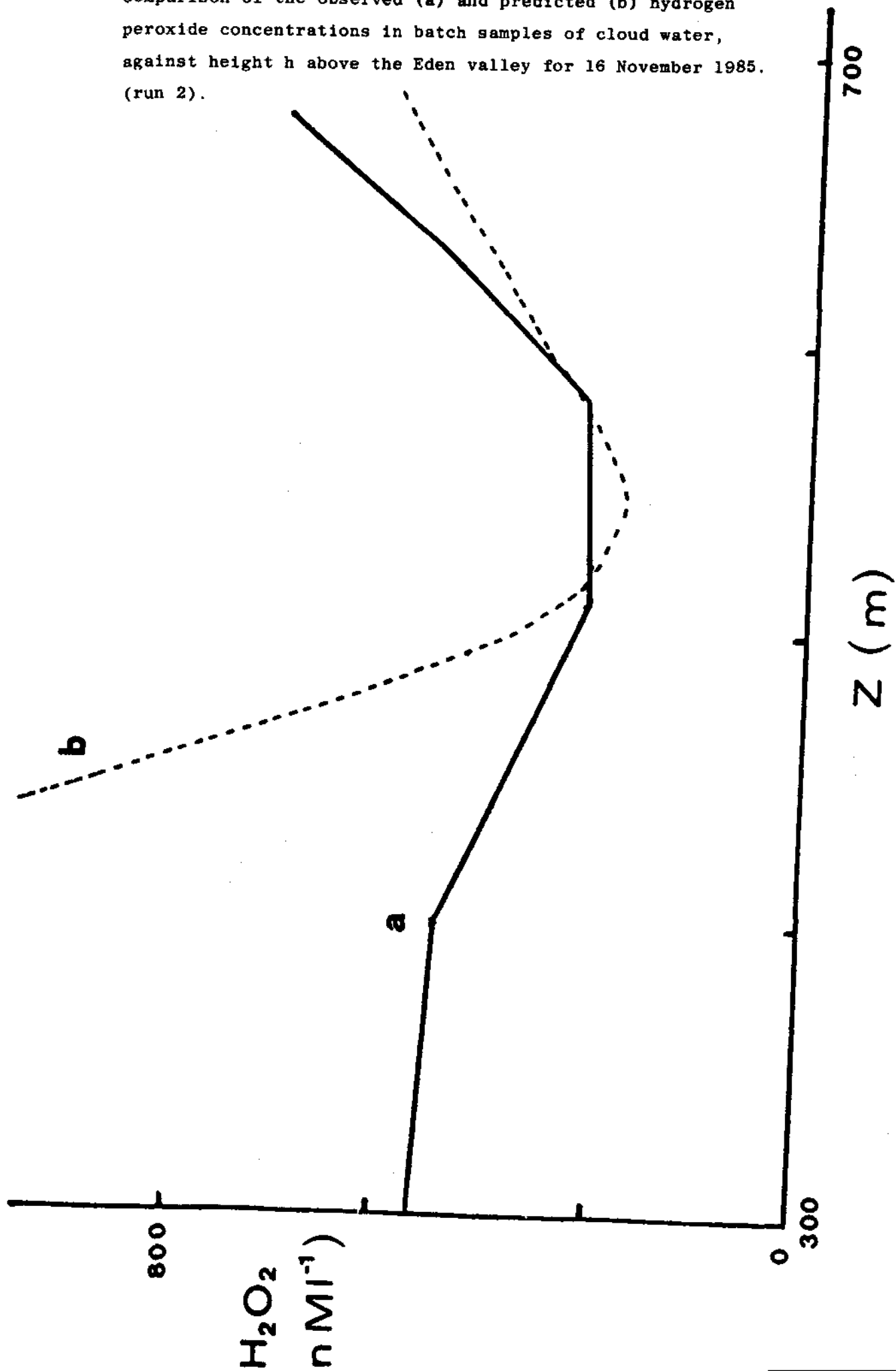


FIGURE 14b

Comparison of the observed (a) and predicted (b) hydrogen peroxide concentrations in batch samples of cloud water, against height  $h$  above the Eden valley for 16 November 1985. (run 2).



SO<sub>2</sub> data for Summit and Wharley Croft sites  
Autumn 1985

FIGURE 15

