INSTITUTE of
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SWAP Modelling Workshop

14-25th September, 1987

Institute of Hydrology

Edited by

Nils Christophersen
and
Paul Whitehead

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PROCEEDINGS FROM SWAP MODELLING WORKSHOP

14-25 September 1987, Institute of Hydrology, Wallingford

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1. INTRODUCTION

The workshop was organized to follow up the recommendations for future modelling work from the SWAP review meeting in Bergen in June 1987. Basically it was agreed in Bergen that future work should start from existing versions of the Birkenes and MAGIC models. The present workshop has concentrated on:

(a) developing models for short term or episodic changes in streamwater chemistry, and

(b) a sensitivity analysis of MAGIC to investigate parametric uncertainty, confidence bounds on trends and regional analysis.

BACKGROUND

From the application of the original Birkenes model to presumably conservative species like Cl and H_2018 (018 for short) it has become apparent that the representation of flow paths within the model needs re-evaluation (Neal et al., 1987; Hooper et al., 1987). Streamwater chemistry shows pronounced variations with flow, while Cl and 018 generally exhibit a strongly damped behaviour. No other hydro-chemical model has so far been subjected to the test of reproducing both conservative and chemically reactive species but this will obviously be needed.

On the chemical side there is strong evidence that the assumption of a single gibbsite equilibrium condition within a catchment should be discarded (Hooper and Shoemaker 1985; Sullivan et al., 1986; Neal 1987, Seip et al., 1987). But also the conventional procedure of using stability diagrams to infer mineral solubility control must be re-evaluated (Neal, 1987). In addition to this, recent work has shown that in some cases it is impossible to identify processes occurring in the terrestrial part of a catchment from observations of streamwater chemistry (Christophersen et al., 1987). This is due to the mixing of water from various soil layers in the stream with subsequent degassing of CO_2 and potentially precipitation of $Al(OH)_3$.

These developments all point to the necessity of re-evaluating hydrochemical modelling of watersheds.

Another major area of concern is the extent to which models can be 'transferred' from catchment to catchment or applied within a regional framework. Results from several applications of MAGIC indicate that there is a consistent pattern of parameter variation (Whitehead et al., 1987). However, a full sensitivity analysis is required to assess parametric uncertainty on both a temporal and regional scale.

2. MODELLING PHILOSOPHY

The basic problems involved in modelling streamwater chemistry were discussed in depth at the workshop. The conceptual picture in Fig.1 was generally agreed upon as a realistic description of water flow paths on hillslopes in acid sensitive areas in Scandinavia and Britain. Water movement during stormflow on slopes with thin soil cover (say 1 m) would be characterized by rather random patterns resulting from the effects of, for example, high variability in hydraulic conductivity including macropores and uneven topography. The net result implies a high degree of mixing on the catchment scale with water moving maybe several times between soil horizons. The irregular patterns on the detailed scale are, however, not reflected in streamwater chemistry which generally shows a regular and predictable behaviour.

The participants agreed on the paramount importance of watershed hydrology in determining the chemical response of a stream to acid deposition. However, many difficulties exist with the construction of a physically-based model of streamflow generation. First, no consensus exists on the dominant processes controlling streamflow generation at the watershed scale. Furthermore, because more than one set of processes are able to reproduce the hydrograph, we cannot be certain that the correct set of processes are contained within the model simply because the model

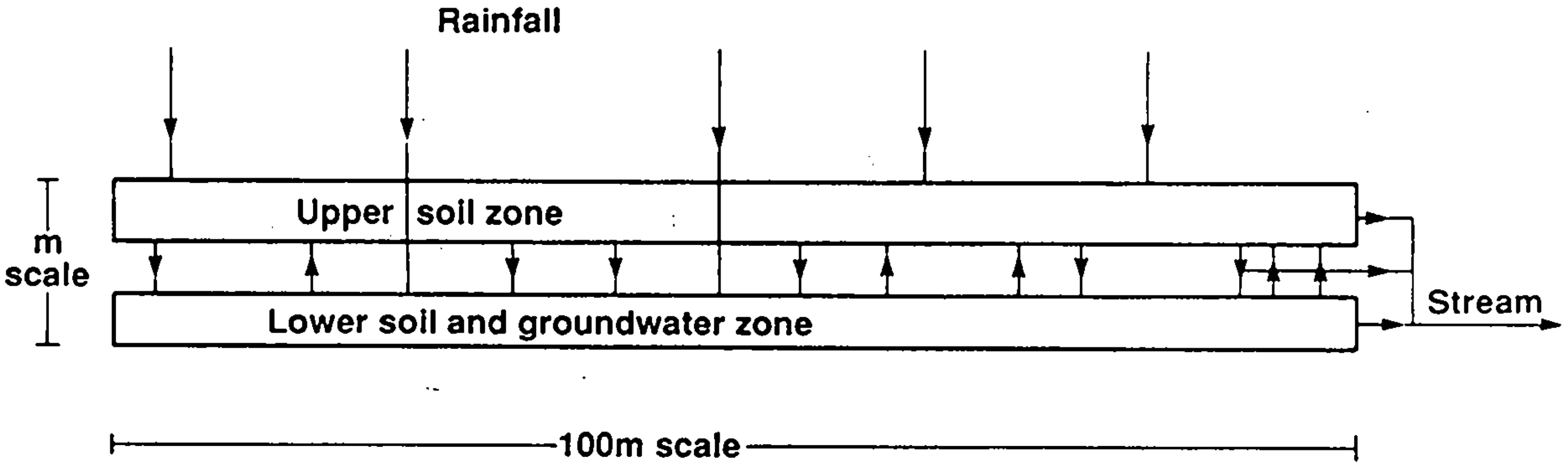

Rainfall
Upper soil zone
m scale
Lower soil and groundwater zone
Stream
100m scale

Figure 1

predictions fit the observed hydrograph. Secondly, even if a set of processes is taken to be correct, the spatial variability of the watershed is at a scale impractical for modelling. Hence the parameters are lumped representations and are therefore still not directly measurable. The data requirements of these models, even if spatially lumped, often exceed the data available from experimental watersheds.

The conclusion of the discussion was that a new hydrologic structure was necessary in the next generation of hydrochemical models. Such models are required to capture the chemically important aspect of waterflow through the catchment (eg. residence time and flow through chemically distinct soil horizons). Because of their artificial nature, the new model structures must be subjected to rigorous statistical analysis to ensure parameter identifiability and stability. It is important that the models are able to reproduce not only the hydrograph but also chemically inert (conservative) tracers as these provide important information on the the mixing patterns in the watershed.

Most probably the regular behaviour of streamwater chemistry can be well reproduced by different models of widely different complexity. However, each approach would emphasize different aspects and an independent observer wishing to understand the detailed processes leading to the observed streamwater chemistry cannot judge which, if any, solutions are closest to reality. Thus it might be appropriate to apply Occam's razor and start from a simple solution given the aims of (1) identify the dominant processes operating, and (2) predict the response in future streamwater chemistry to anthropogenic impacts such as acid rain and land use changes. In our view, one challenge to the modelling work lies in striking the balance between meeting these two requirements while retaining a reasonably simple picture. The role of soil measurements and plot studies would be to limit the possible chemical submodels and give ranges for the parameters involved.

It was agreed that future model structures must fulfil a set of necessary conditions in order to be considered promising:

(a) Parameter identifiability

This means that for a given data set there must exist a unique set of parameter values that produce a best fit of the model. A combined test involving both artificial and real data is probably useful here (de Grosbois et al., 1987; Hooper et al., 1987). In the present Birkenes model one of the parameters (AMIN) is hard to identify from streamwater observations.

(b) An ability to reproduce all signals

This includes flow, the major chemically reactive species, and at least one conservative species which could be Cl but preferably 018 or deuterium if available.

(c) Parameter consistency

When calibrated for a given period the same parameter values must give acceptable fits for other periods. The term "acceptable" has yet to be defined but could, for example, be set as an allowed decrease in R^2 or in the objective function compared to the optimal fits for the other periods.

(d) Benchmark testing

This means that the model must reproduce a given signal at least as good as "black box" approaches involving, for example, regression or time series techniques.

The resulting model structures passing these tests must then be subject to an evaluation of both parameter uncertainties as well as structural uncertainties.

3. WORKSHOP AIMS

In addition to identifying dominant mechanisms and being used for predictions, an important part of the modelling work within SWAP is to aid in the planning of experimental work and data quality control. Within this framework it was agreed to pursue three goals in parallel at the present workshop. Firstly, development should start on a new model structure based on the present Birkenes model. Secondly, it was decided to continue application of the existing model with emphasis on flow, Cl, and 018 to Birkenes, Allt a Mharcaidh, Llyn Brianne and Plynlimon. Treatment of sulphate and the cations will be taken up the next workshop. The applications would be carried out using an automatic calibration routine to quickly explore the potential of the model (de Grosbois et al., 1987; Hooper et al., 1987). Thirdly a sensitivity analysis of MAGIC would be conducted to assess parameter uncertainty and produce confidence bounds on historical and predicted trends. The model would also be applied in a regional analysis to the Galloway area making use of the extensive databases that exist to assess model performance.

4. APPLICATIONS OF THE BIRKENES MODEL

Birkenes

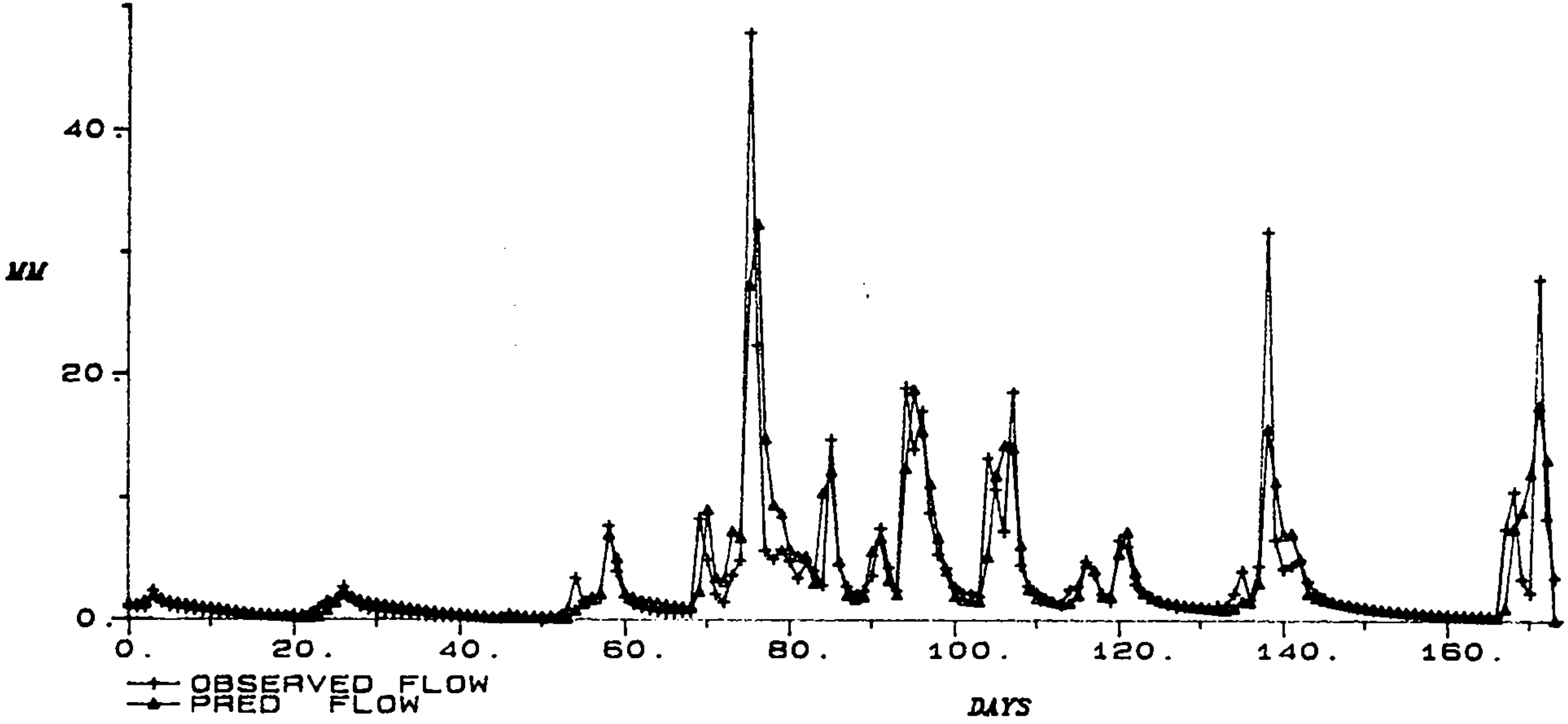
Extensive work has recently been undertaken on modelling both flow and 018 for this catchment covering the years 1983 and 1984 (de Grosbois et al., 1987; Hooper et al., 1987). Data for 1985 have recently become available and the model applied to all 3 years using an updated version of the optimization program. Figures 2 and 3 show the results for 1985 in a run where the 018 signal was weighted 20 times as heavy as the flow. One can see that peak flows are typically underestimated by the model and that discrepancies exist between observed and simulated 018. Putting less weight on 018 will only slightly improve the simulated flow.

Allt a Mharcaidh

Only flow simulation was carried out for this catchment using data from the snow-free season of 1986. The initial results indicate that further work is required in the following areas:

(1) the stage - flow relationship at high flow is uncertain and needs further assessment;

(2) the Allt a Mharcaidh area is about 10 km^2 which is over 20 times the size of Birkenes. In such a large catchment the routing of water



Birkenes Model BSIZE

Flow & 018 (1:20)L

Lambda = .4

Figure 2

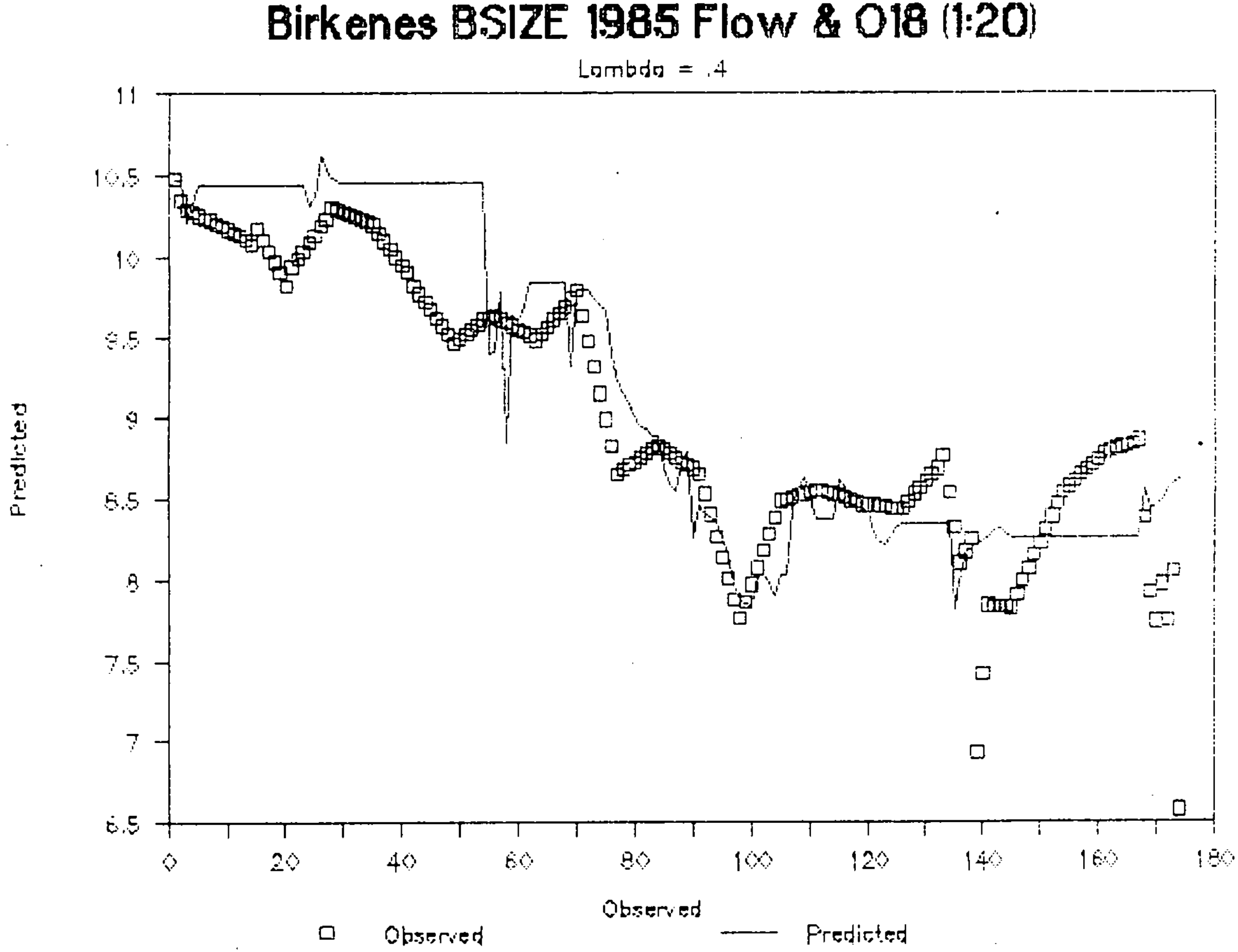

Birkenes BSIZE 1985 Flow & O18 (1:20)
Lambda = .4
Predicted
11
10.5
10
9.5
9
8.5
8
7.5
7
6.5
0
20
40
60
80
100
120
140
160
180
Observed
□ Observed
Predicted

Figure 3

could become more important and deserve separate treatment in a future model. This also argues in favour of trying to model the two subcatchments before going to full area.

018 data will soon be available for this catchment and will be included in future work.

Plynlimon, Afon Hafren

The Birkenes model has been applied to this catchment previously in an attempt to model flow and Cl (Neal et al., 1987). The hydrograph was very well reproduced but the observed damped response in streamwater Cl was impossible to reproduce. Similar results were obtained at the workshop when modelling flow and 018 (Figures 4 and 5).

At Plynlimon precipitation is collected weekly and questions were raised concerning possible isotopic enrichment in the collectors. This could explain part of the model's deviations during the dry summer period. But the main point seems to be that the Plynlimon catchments exhibit a rather extreme degree of damping in 018 and Cl although chemically reactive species like H^+ and Al show drastic changes with flow (Neal et al., 1986). The current model structure was determined to be inadequate to describe the behaviour of 018 in this catchment. The large size (4 km^2) of the catchment may also play a role.

Llyn Brianne (LI 1)

For this catchment the model was able to reproduce the flow well (see Figure 6). No isotopic data are available so Cl was used and treated as a conservative element, but the model again proved unable to respond in the damped manner of the stream in response to a highly variable Cl input. (It should be noted that recent results from Llyn Brianne suggest significant stream chloride variation during sea salt events).

Conclusions of Applications

The hydrology is adequately reproduced at all catchments. There is a tendency to underpredict peak flows, but that is not unexpected with this simple model structure.

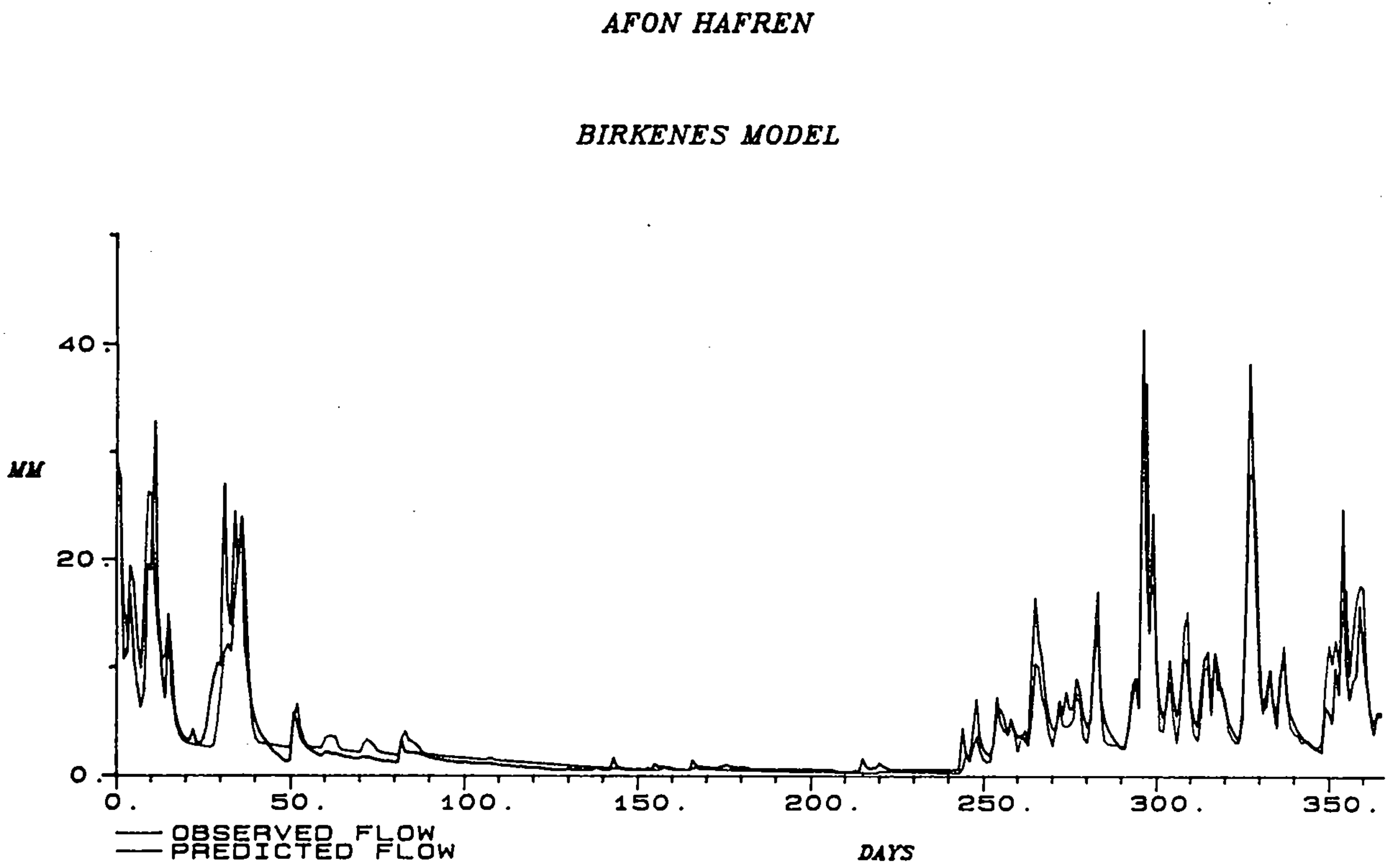

AFON HAFREN
BIRKENES MODEL
MM
40.
20.
0.
0.
50.
100.
150.
200.
250.
300.
350.
DAYS
OBSERVED FLOW
PREDICTED FLOW

Figure 4

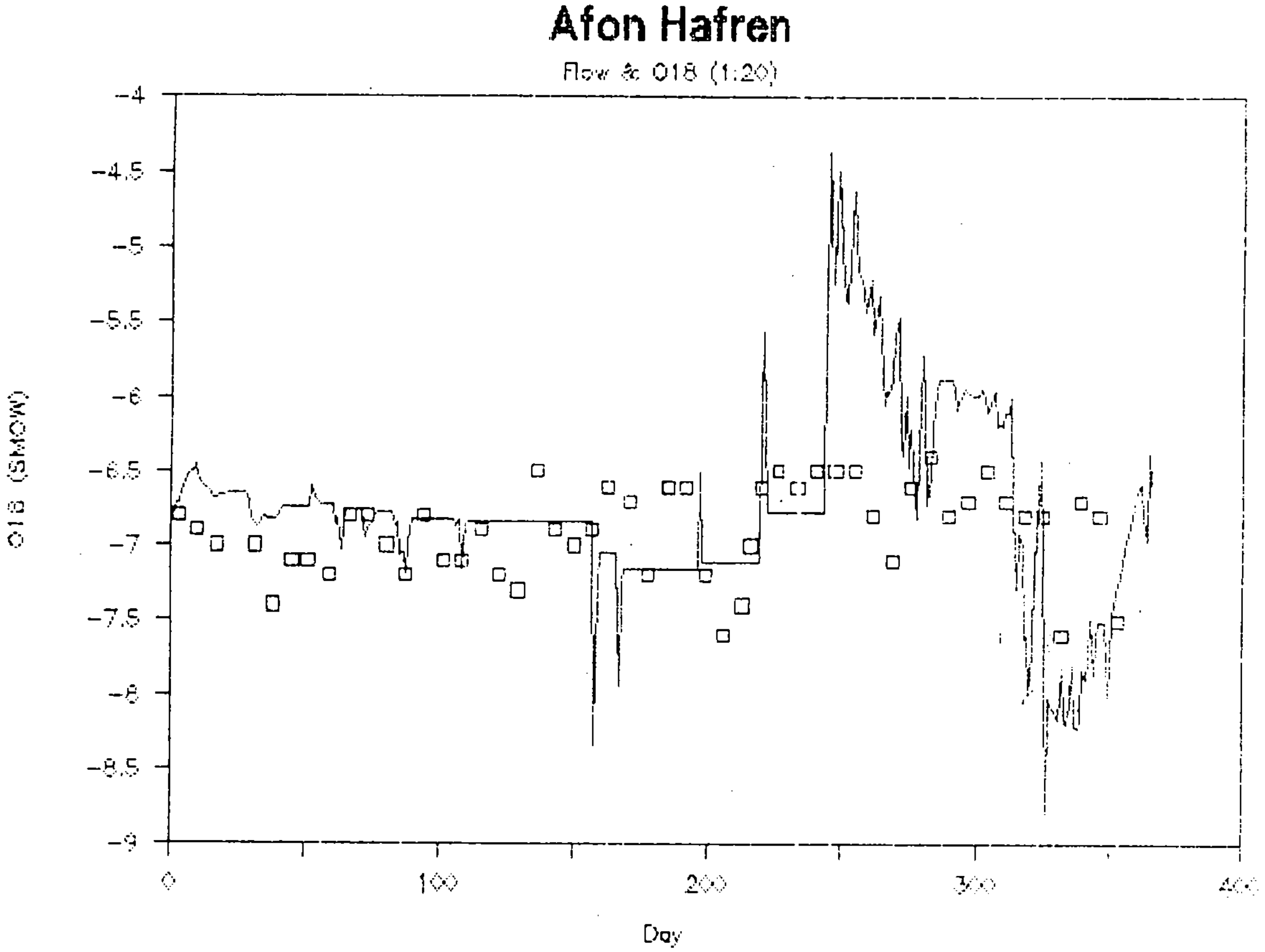

Afon Hafren
Flow & O18 (1:20)
O18 (SMOW)
-4
-4.5
-5
-5.5
-6
-6.5
-7
-7.5
-8
-8.5
-9
0
100
200
300
400
Day

Figure 5

LLYN BRIANNE

1st *APRIL* 86 *TO* 30th *SEPTEMBER* 86

BIRKENES MODEL

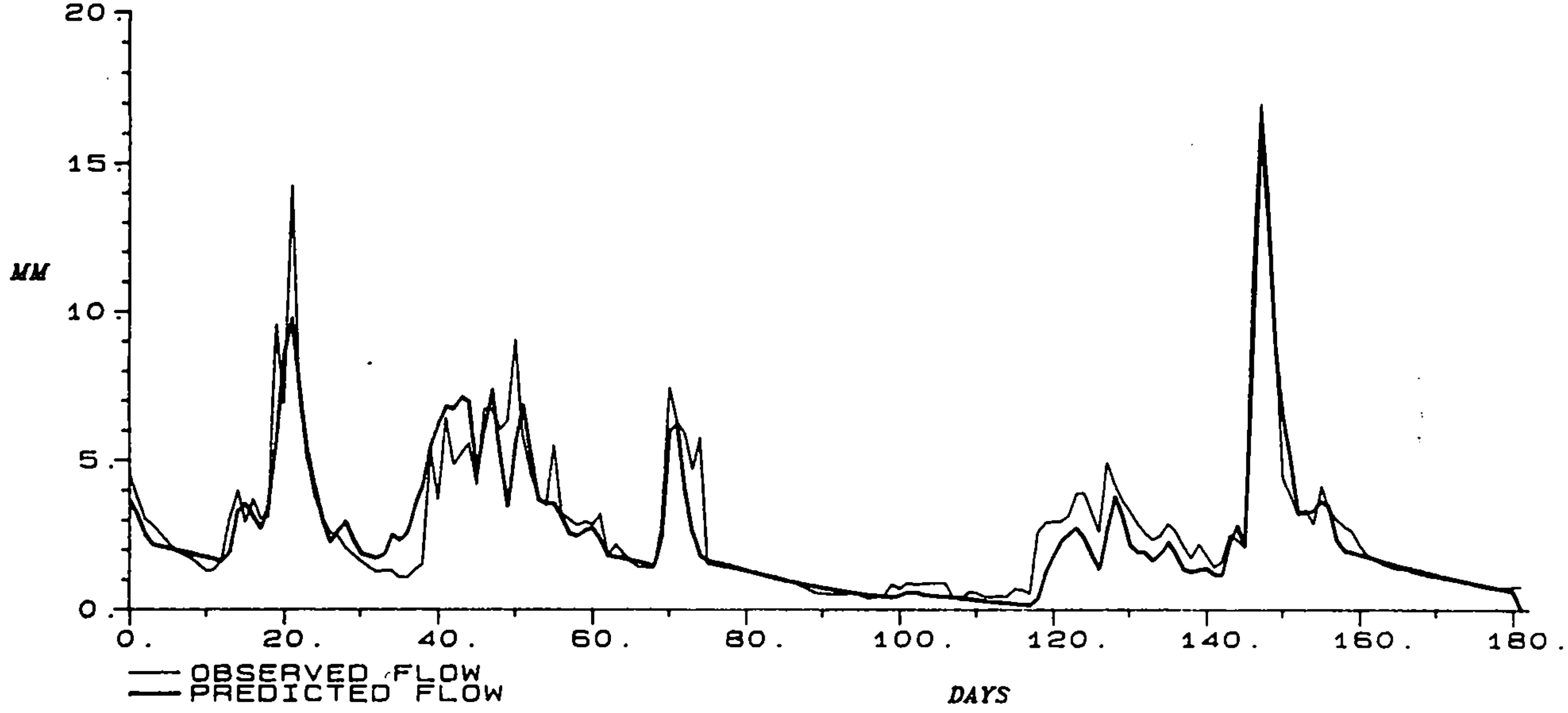


Figure 6

There is also some question as to the conservative nature of chloride as is evident from the Plynlimon and Llyn Brianne catchments. The role of vegetation in changing the Cl input was discussed based on evidence from the Allt a Mharcaidh. 018 is likely to be a better tracer than chloride.

New Model Structures

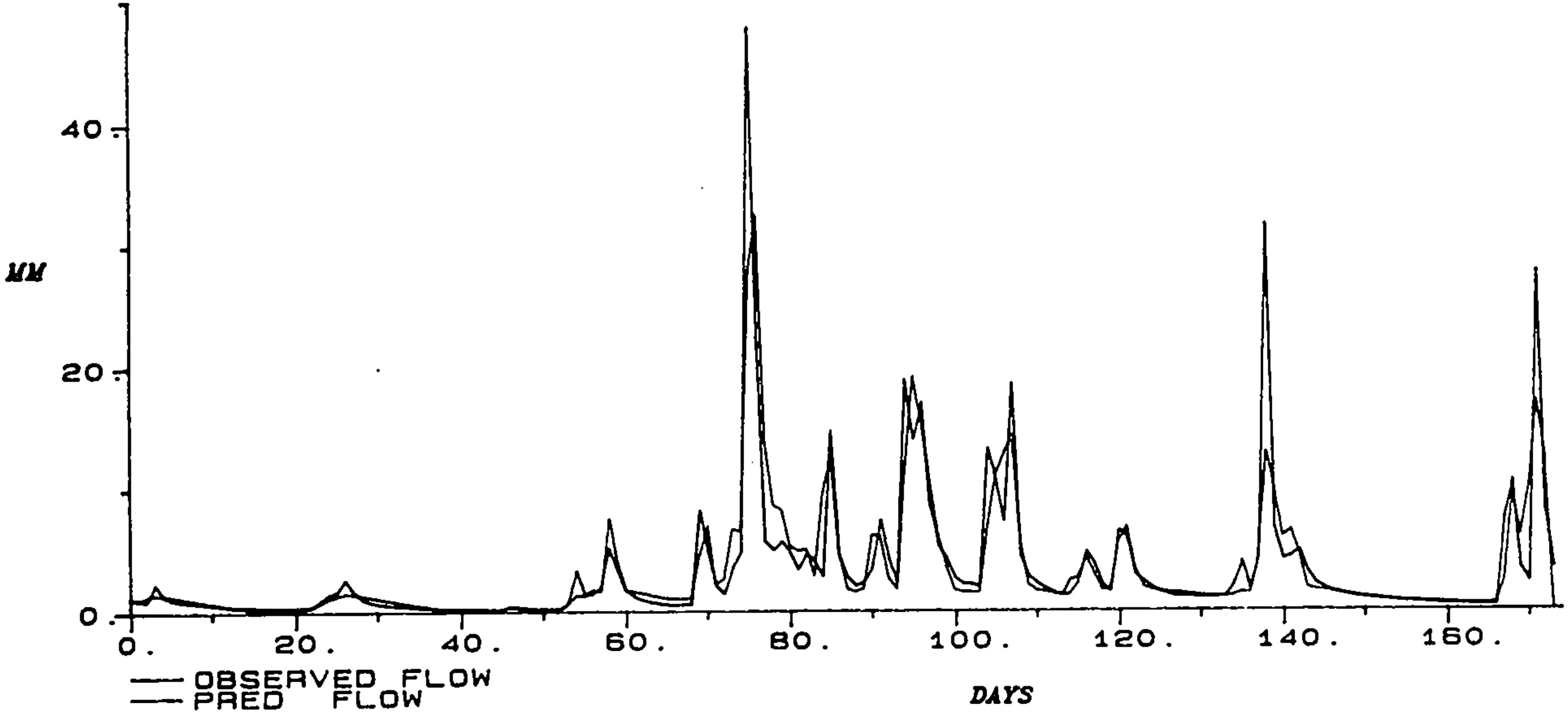
Several new model structures were discussed at the workshop. Given the problem with overparameterization of the Birkenes model and the stated goal of starting from the simple, a one-box structure was taken as the first version in a new modelling effort. Hydrologically the box is well mixed implying that conservative species are given a uniform concentration. Chemically the model can be divided into distinct layers corresponding to a podzol horizon . So far the hydrologic, 018, Cl, and sulphate portions have been programmed. For sulphate two layers have been chosen corresponding to an organic and mineral horizon, respectively. The sulphate reactions are at present simplified versions of the reactions in the Birkenes model.

Results from Birkenes for flow and 018 for 1985 are given in Figures 7 and 8. Compared to the results for the Birkenes model (Figures 2 and 3) it is seen that the one-box model gives a very similar simulation of flow but a better representation of 018. For the other years the one-box structure is better or at least not worse than the Birkenes model. The results so far are encouraging.

On the cation side the reactions to be included will be cation exchange and weathering. It was agreed that soil water chemistry should be used for calibration not streamwater. The model should correctly mix these soil solutions to predict the stream chemistry. Some theoretical work is needed here on the mathematical side to cast the equations in the right framework. Irrespective of the final hydrologic structure chosen these reactions are believed to be common to most acidification models.

5. SENSITIVITY ANALYSIS APPLIED TO MAGIC

The MAGIC model has been used to simulate long term changes in stream chemistry in two Scottish catchments, Loch Dee and Round Loch of Glenhead.



Onebox Model

Flow:018 (1:20)

Lambda = .4

Figure 7

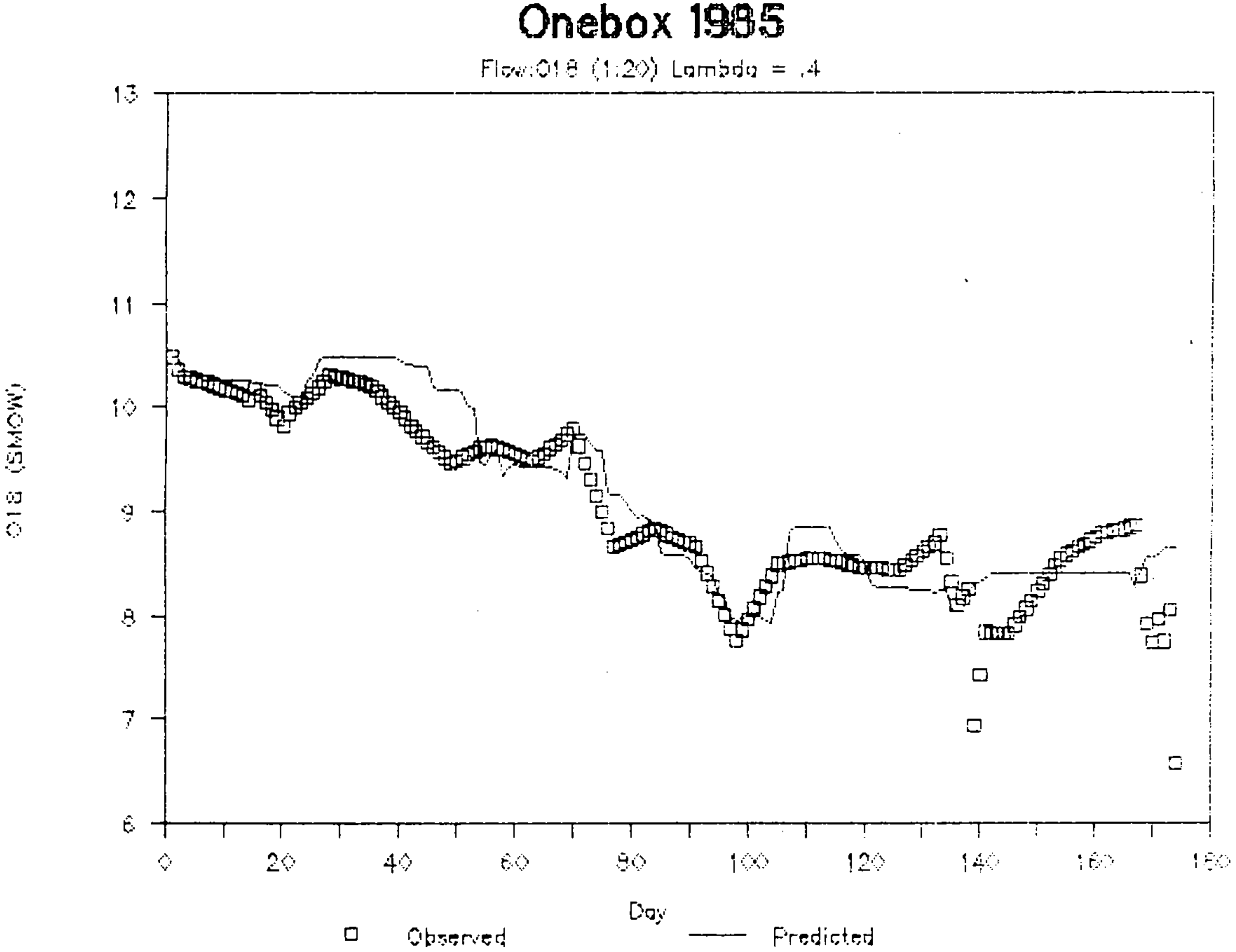

Onebox 1985
Flow:O18 (1:20) Lambda = .4
13
12
11
10
9
8
7
6
O18 (SMOW)
0
20
40
60
80
100
120
140
160
180
Day
□ Observed
—— Predicted

Figure 8

A Monte Carlo analysis has been used in conjunction with MAGIC in an attempt to place confidence bounds on the stream water chemistry variables through time. Figures 9 and 10 show the results for Dargal Lane (a subcatchment of Loch Dee) and Round Loch of Glenhead. In both cases the 95% confidence bounds from MAGIC are very similar to the error bands suggested by Batterbee from the palaeocological analysis (approximately 1-1.5 pH units). In case of Round Loch the MAGIC pH simulation is very similar to the pH reconstruction from the palaeocological analysis. Note that the Dargal Lane simulation results suggest a slight recovery in recent years and this agrees with recent findings by Batterbee. Further details of this work are available in Appendix I.

6. REGIONAL ANALYSIS OF MAGIC

MAGIC has also been applied to Galloway region of south west Scotland. The procedure is to specify parameter ranges that might be expected from the wide range of catchment types and to simulate using Monte Carlo analysis the ensemble behaviour across the region. From this analysis the simulated distribution of water quality across the region can be compared with the observed distributions of water quality. Over 400 survey samples exist for Galloway giving a representative picture quality across the region. Figures 11-13 show the simulated and observed distribution for pH, sulphate and Ca. The fit is extremely good and it is suggested that MAGIC is capturing the principal changes over the region. The model can be used to reproduce distributions that existed prior to anthroprogenic pollution and as shown in Figures 14 and 15 indicate that significant changes have occurred. Appendix II contains a draft paper describing this research in detail.

7. FUTURE WORK

A timetable was developed for future work.

Birkenes Model

December 1987:	Statistical evaluation of the one-box structure; evaluation of sulphate sub-model.
March 1988:	Completion of mathematical (theoretical) framework for

Figure 9 DARGALL LANE SIMULATION

pH

(mean and 95% confidence levels)

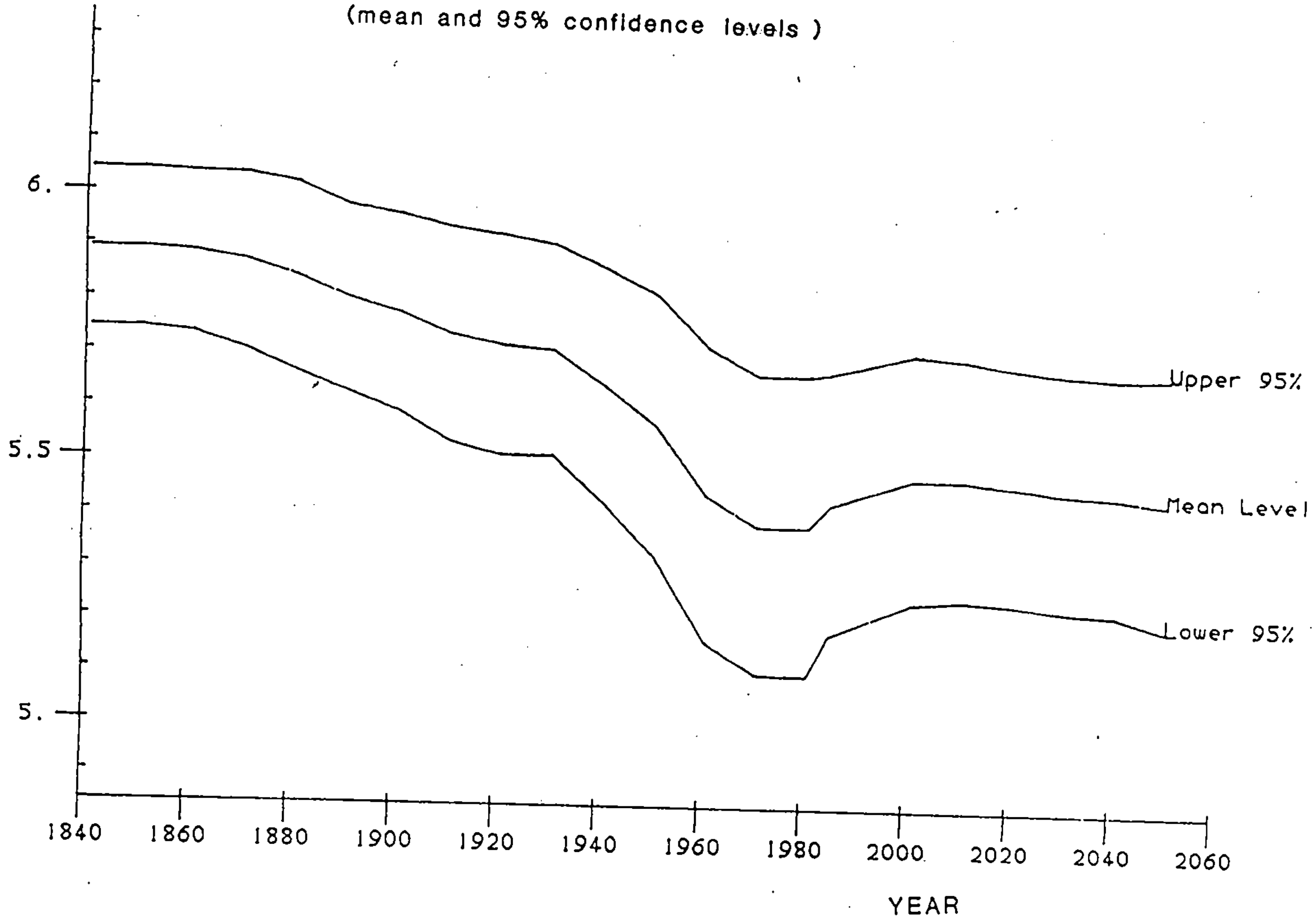


Figure 10 ROUND LOCH OF GLENHEAD SIMULATION

COMPARISON WITH PALAEOECOLOGICAL RESULTS

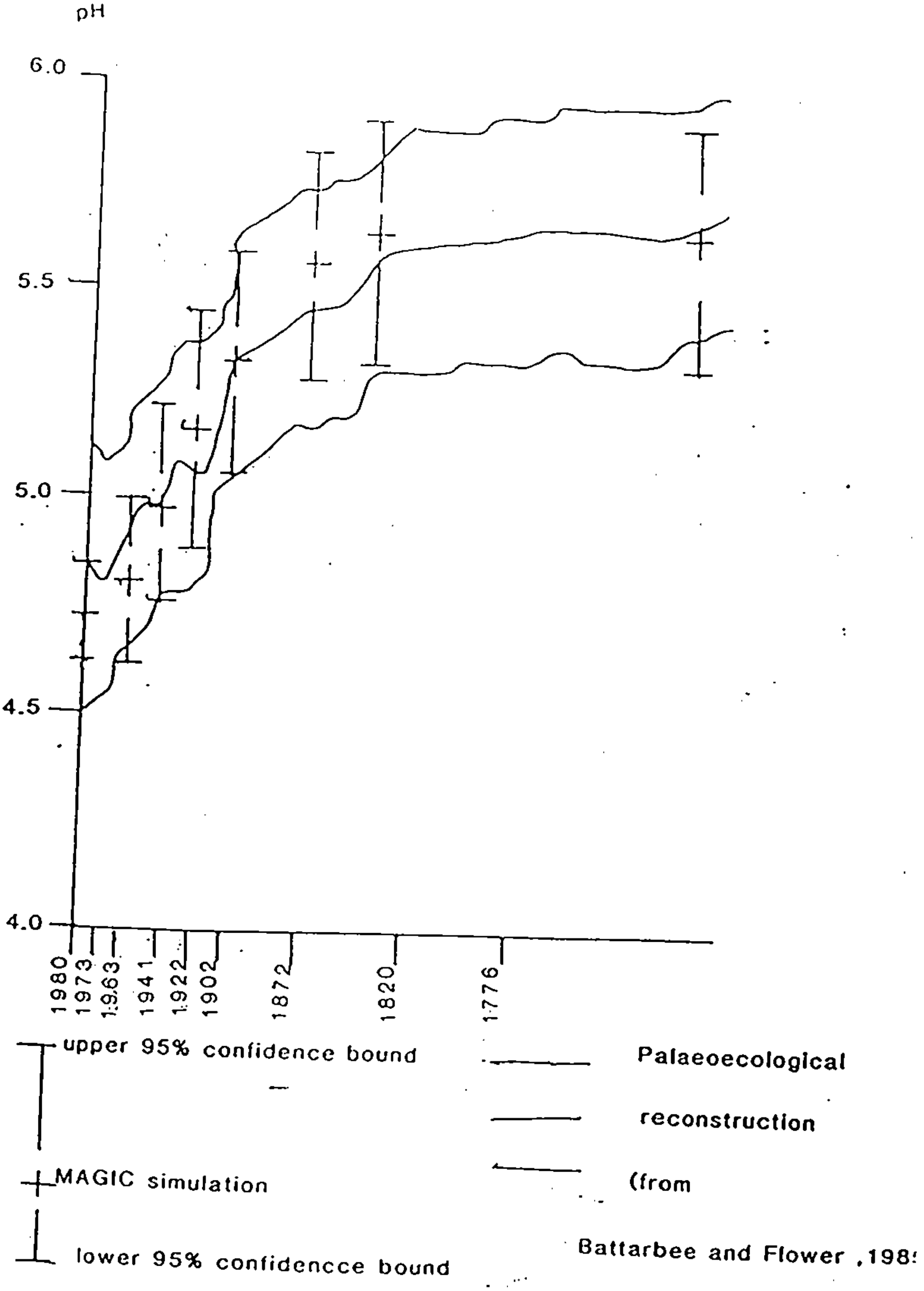
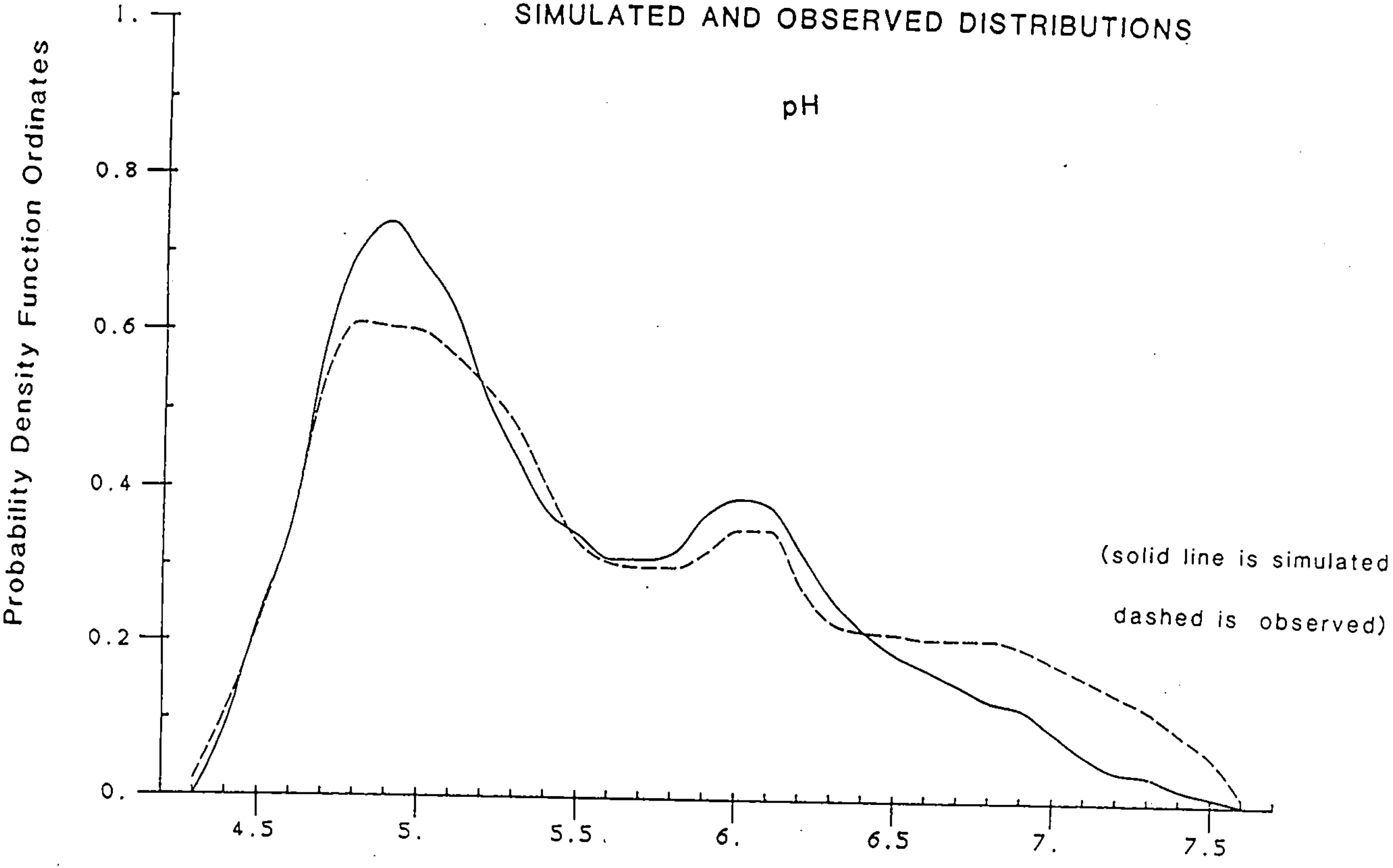


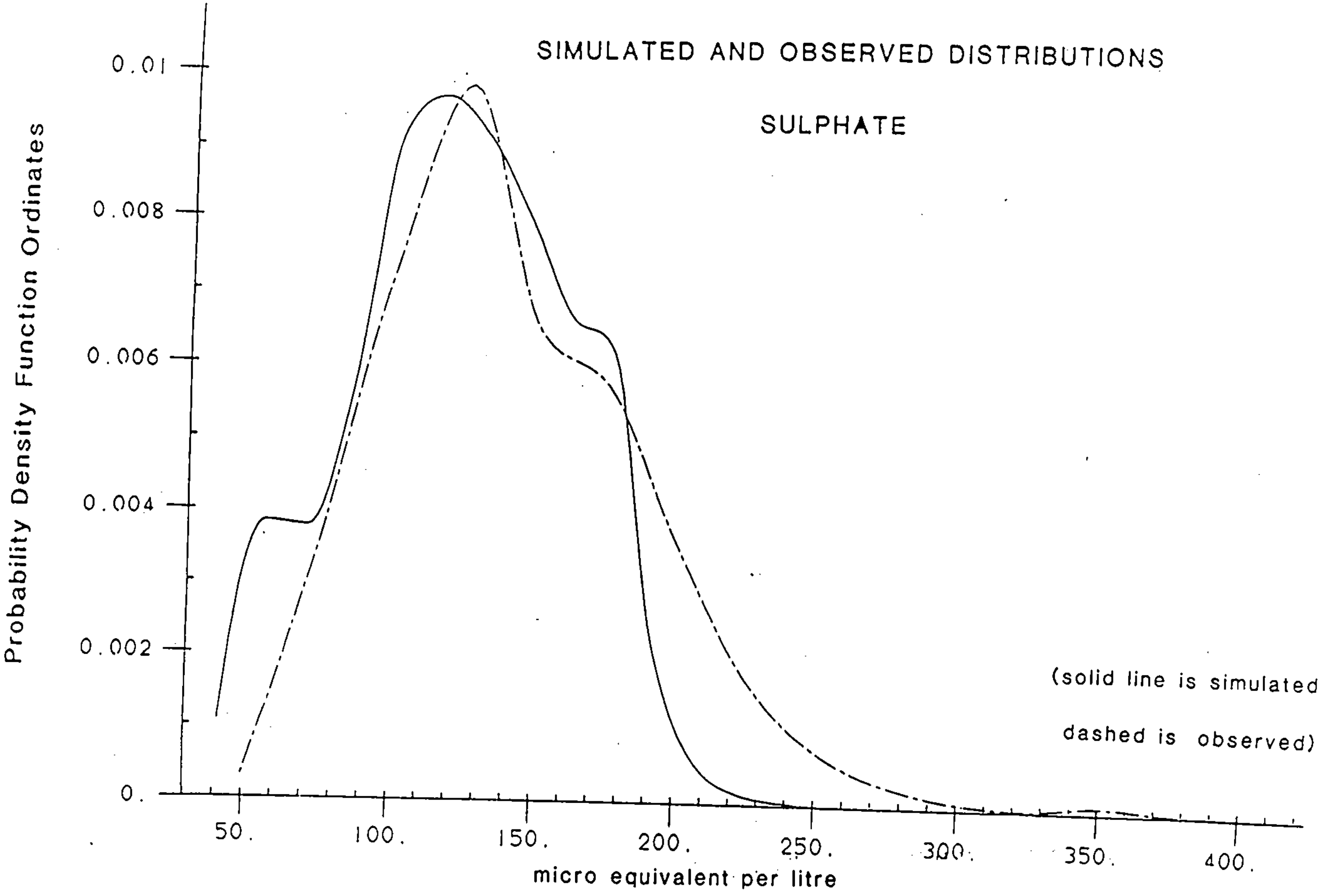
FIGURE II CLUSTER 1



SIMULATED AND OBSERVED DISTRIBUTIONS

pH

FIGURE 12 CLUSTER 1

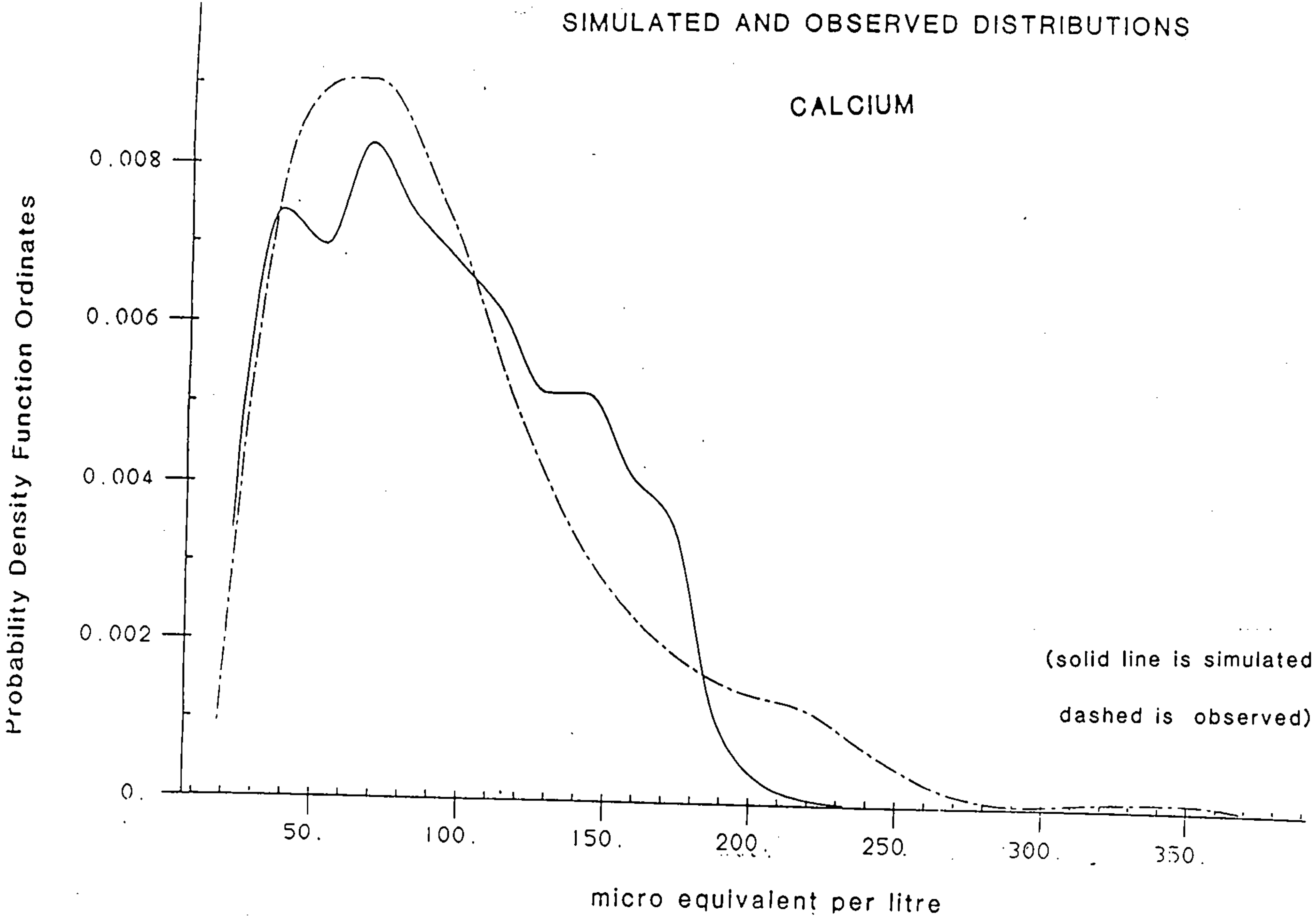


SIMULATED AND OBSERVED DISTRIBUTIONS

SULPHATE

(solid line is simulated
dashed is observed)

FIGURE 13 CLUSTER 1



SIMULATED AND OBSERVED DISTRIBUTIONS

CALCIUM

FIGURE 14 SIMULATION OF CLUSTER 1

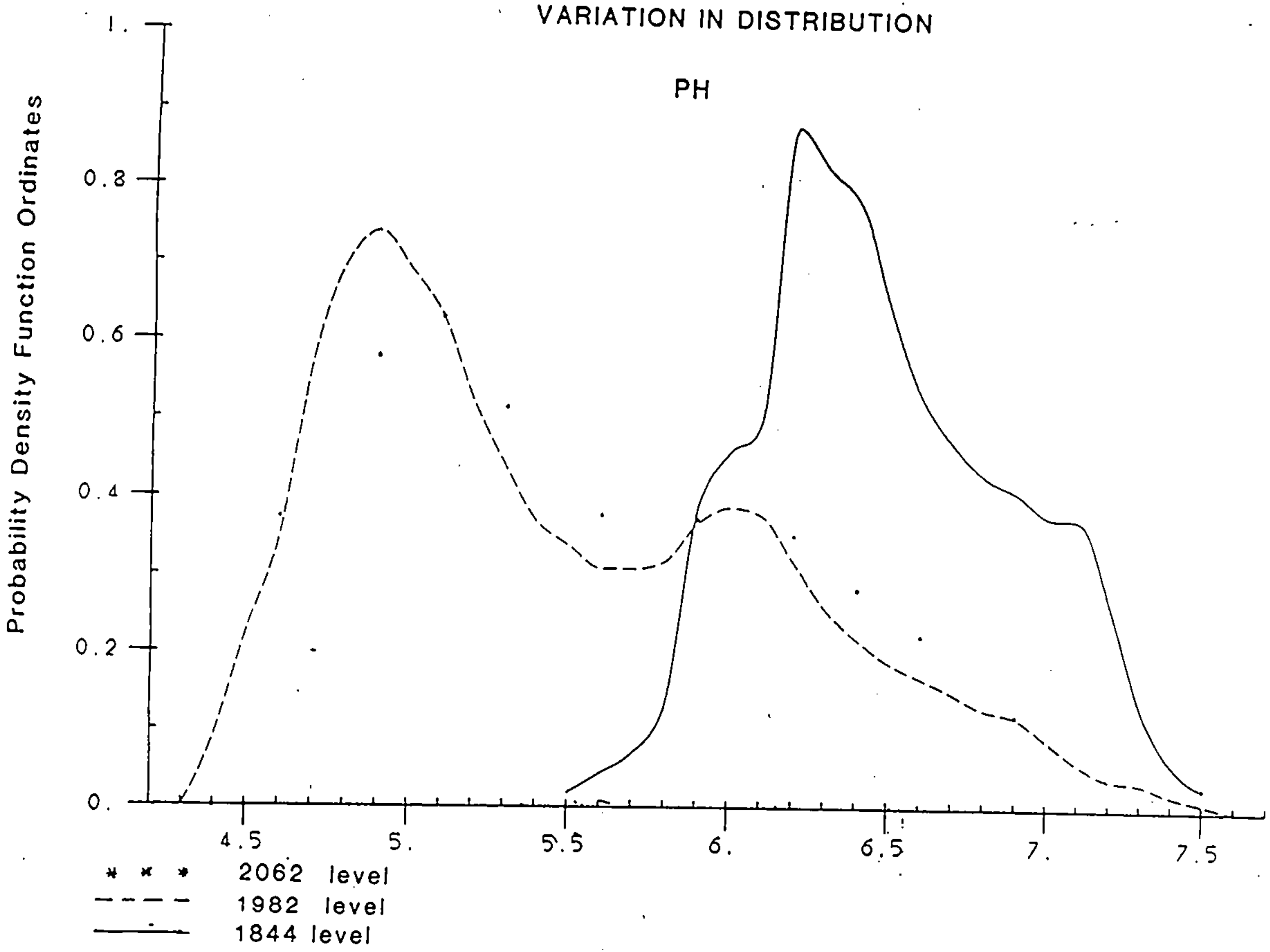
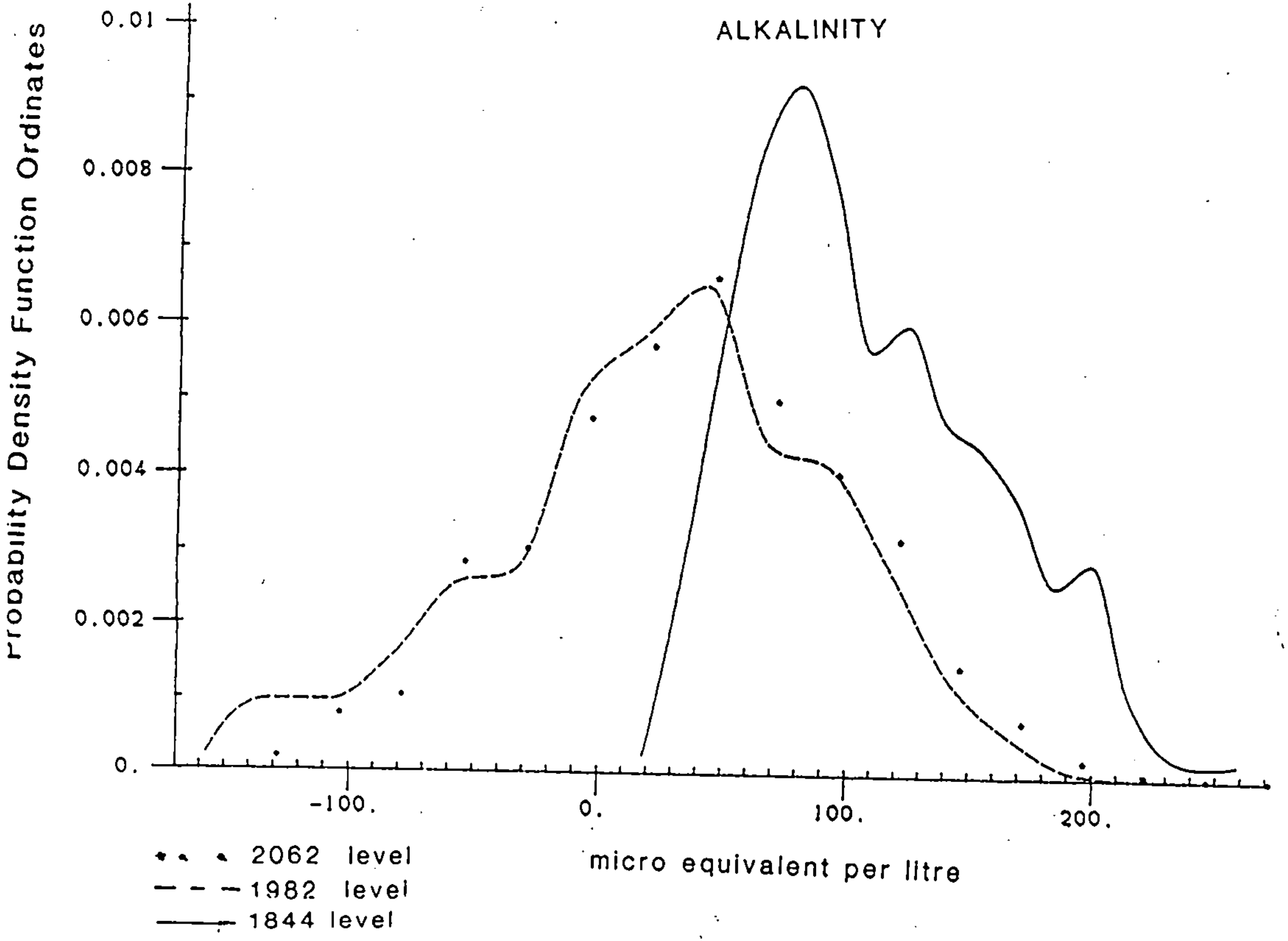


FIGURE 15 SIMULATION OF CLUSTER 1

VARIATION IN DISTRIBUTION

ALKALINITY



revised cation model.
April 1988: Model Assessment (at workshop).
September 1988: Model applied to all SWAP catchments.
December 1988: Evaluation of model results for all catchments.

Baseline model versions should be established and each institute will keep a record of all modification and developments. Exchange of program code will take place through data networks.

MAGIC

December 1987: 2-layer version of MAGIC applied to Allt a Mharcaidh.
March 1988: Application of MAGIC to sites in Wales for detailed comparison with palaeocological analysis.
May 1988: Regional analysis of MAGIC to Wales

COUPLED BIRKENES AND MAGIC MODEL

A linking of these two models has been discussed for some time. MAGIC would be used to compute long term changes in soil chemistry and at selected points in time the Birkenes model would use the soil data from MAGIC as an input and simulate episodic chemistry. Dick Wright of NIVA would take initial responsibility for this effort.

Semi-Distributed Models

The topography of the catchments control the flow paths and hence hydrological response of a catchment. The semi-distributed model TOPMODEL is currently being applied to the Llyn Brianne and Allt a Mharcaidh catchments and will be used to provide useful information for other hydrological and chemical models.

Lake Modelling

IH will survey existing lake models and select one for application in SWAP. In late 1988 this will be coupled to the streamwater chemistry model.

Future co-operation

It was agreed to hold a workshop hosted by the US Geological Survey in Atalanta (pending funding through NATO). Also Jack Cosby, Dick Wright and George Hornberger would be visiting IH in January, 1988. Imperial College would hold a workshop in June 1988.

8. LIAISON WITH IMPERIAL COLLEGE TEAM

A meeting was held with Imperial College colleagues in which their work was presented. Future collaboration will emphasize work on an hourly model version which Imperial has applied to Loch Ard.

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APPENDIX 1

SENSITIVITY ANALYSIS OF MAGIC APPLIED TO TWO SCOTTISH CATCHMENTS

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ABSTRACT

The MAGIC model is used to simulate long term changes in stream chemistry in two scottish catchments. Both catchments are in areas that are sensitive to acid deposition. The simulations are compared to palaeoecoligical reconstructions of stream water pH within the catchments and to present levels of stream water chemistry. A Monte Carlo analysis is used in conjunction with MAGIC in an attempt to place bounds on the stream water chemistry variables through time. A generalised sensitivity analysis is performed, using the results of the Monte Carlo analysis, in order to gauge the relative sensitivity of the model simulation to each parameter.

INTRODUCTION

Evidence exists for the acidification of parts of upland Britain. Battarbee et al. (1985) and Flower and Battarbee(1983) present palaeoecological evidence that the level of pH in several lochs in south west Scotland has decreased significantly during the past 130 years. Stoner et al(1984), Harriman and Wells(1985)and Harriman and Morrison(1981) also suggest increasing levels of acidification as an explanation for the declining fish populations from streams and lakes in Scotland and Wales. The cause of acidification is not fully known but is believed to stem from acid deposition. The processes within the soil that are affected by acid deposition are multifarious and complex. The relative importance of each process is dependent upon the characteristic features of the soil within each catchment. For example the cation exchange capacity and the sulphate adsorption ability are both strongly dependent upon the soil type present within the catchment. Mathematical models of the soil behaviour and response can provide a method of testing hypotheses about the importance of the different processes and can provide clues to help identify the key mechanisms of response to acid deposition for each catchment.

The MAGIC model is a lumped parameter simulation model of long term changes in streamwater chemistry in catchments. It represents five soil processses commonly held to be fundamental to explaining the mechanism of acidification. These are: 1) Cation exchange in the soil; 2) Anion retention by the soil; 3) Aluminium mobilisation; 4) Mineral weathering; and 5) Carbonic acid dissociation as a result of CO_2 held under elevated partial pressure in the soil, (Cosby et al., 1985a). The MAGIC model has been applied to a variety of catchments (e.g. Cosby et al., 1986a Wright et al., 1986, Whitehead et al., 1987) and a sensitivity analysis of the model to variation in the model parameters and to the soil processes has been performed by Hornberger et al (1986). Cosby et al (1986b) have previously calibrated the model to the Dargall Lane subcatchment of Loch Dee situated in an acid sensitive area (Wright and Henrikson, 1979). No account is taken of the role of organic acids in the model and for this reason this we focus here upon a region in which strong acids are the dominant acidifier. This analysis aims to simulate the chemistry of the Round Loch of Glenhead and of Dargall Lane and to match the palaeoecological records of Battarbee and Flower (1985) of pH in time and the observed levels of present day chemistry (Burns et al., 1984 and Harriman et al., 1986). By use of the Monte Carlo method it is hoped to find regions of confidence for the simulated variables and to trace these through time. Finally it is hoped to use the Generalised sensitivity technique, developed by Spear and Hornberger (1980), to identify those parameters that are most important in enabling the model to reproduce the observed behaviour of the catchments by comparing those simulations from the Monte Carlo analysis that gave a good match with those that did not.

THE MAGIC MODEL

MAGIC is a mathematical model for simulation of soilwater and streamwater chemistry in catchments. It incorporates five key chemical mechanisms of acidification in soils. These mechanisms stem from the following five soil processses: 1) Alkalinity generation in soil water; 2) Dissolution of Aluminium minerals in soils; 3) Cation exchange by soils in the catchment; 4) Mineral weathering of the soil; and 5) Retention of anions in soils. Alkalinity is generated by the formation of bicarbonates when carbon dioxide, under high partial pressure in soil, dissolves with the soil water

$$CO_2 + H_2O = H^+ + HCO_2- \qquad (1)$$

Soil aluminium chemistry is assumed to be controlled by the equilibrium of a solid phase of $AL(OH)_3$ with free hydrogen ions

$$3H^+ + AL(OH)_3(s) = AL^3+ + 3H_2O \qquad (2)$$

This reaction releases aluminium ions which may form aqueous complexation with flouride, sulphate or hydroxide or may instead exchange place with the base cations present on the soil matrix cation exchange sites. The complexation reaction equations in the model include corrections for temperature and for ionic strength.

$$AL^{3+} + 3BCX(s) = ALX_3(s) + 3BC^+ \qquad (3)$$

In general the trivalent aluminium ions are retained by the soil matrix in preference to the monovalent or divalent base cations. The cation exchange equilibria are evaluated using Gaines-Thomas expressions (Gaines and Thomas, 1953):

$$SALBC = \frac{(BC^{2+})^3\ E^2al}{(AL^{3+})^2\ E^3bc}, \quad \text{or } SALBC = \frac{(BC^+)^3\ Eal}{(AL^{3+})\ E^3bc} \qquad (4)$$

for divalent and monovalent base cations respectively. The brackets denote aqueous activities and the SALBC is a selectivity coefficient (Reuss, 1983) and the Eyy indicates fractions of the appropriate ion on the soil cation exchange matrix.

Thus

$$Eyy = \frac{(Y)}{CEC}$$

where CEC is the cation exchange capacity of the soil (meq/kg).

The first three processes form the equilibrium part of the model and is based on the simple conceptual model of Reuss and Johnson (1985). This is extended to allow for variation in all of the important cations and anions and also includes the aluminium dissolution and complexation (Cosby et al, 1985b). Equations 1-4 are further utilised to determine stream water concentrations from the soilwater concentrations. Carbon dioxide partial pressure is released to the atmosphere at the stream channel and the equilibrium of equation 1 shifts to the left. The base cation exchange reactions are assumed not to occur in the stream where there is no contact with cation exchange sites. The remaining two soil processses enable dynamic simulation by coupling the equilibrium model with dynamic mass budgets for each of the base cations and strong acid anions in the soil model (see Cosby et al., 1985a)

$$\frac{dYt}{dt} = Fy + Wy - Q*(Y)*C \qquad (5)$$

where Yt is the total amount of ion Y in the catchment (eq/m^2)

Fy is the atmospheric flux of ion Y into the catchment (meq/m^2/time)

Wy is the net uptake flux of ion Y(eq/m^2/time)

(Y) is the molar concentration of the free and complexed ion in stream water.

Q is the volume flow of the stream(m^3/time)

C is the charge of the ion

The sulphate dynamics of the model are based on sulphate adsorption by the soil. This is assumed to be reversible an is modelled by a Langmuir isotherm:

$$Es = Emx*(SO_4)/(C+(SO_4)) \qquad (6)$$

where Es is adsorbed sulphate(meq/kg)

(SO_4) is the concentration of dissolved sulphate (μeq/l)

Emx is the maximum adsorption capacity(meq/kg)

C is the half saturation constant(μeq/l)

The acid anions in the model are linked to the base cations by a charge balance for the soil water which is assumed to have zero net charge. Thus the movement of strong acid anions (i.e. SO_4,CL,NO_3 and F) through the soil is accompanied by a leaching of base cations from the soil. The major effects of acid deposition on surface water quality in catchments are believed to be decreased pH and alkalinity and increased base cation and aluminium concentrations. The model broadly reproduces these responses (Cosby et al., 1985a, Neal et al., 1986).

MONTE CARLO SENSITIVITY ANALYSIS

By ignoring heterogeneity within the catchment, lumped parameter water quality models are susceptible to uncertainty of parameter estimation. Often, however, knowledge of the geological and hydrological characteristics of a catchment can allow upper and lower limits to be placed on the values that the model parameters are likely to take. These parameter ranges may be built into the models using the Monte Carlo method (e.g. Brutsaert, 1975 or Whitehead and Young, 1979, Hornberger and Spear, 1980). This is an artificial sampling method in which a priori probability density functions are assigned to relevent parameters. These functions are usually either rectangular or triangular, reflecting the limited knowledge of the actual spatial distribution of the parameter in the catchment. An ensemble of systems is defined by a given model structure and set of a priori distributions. The model of the actual system is assumed to be a random member of the ensemble. The set of model systems is randomly sampled and the model is run. This is repeated until a collection of simulations is gathered whose statistical properties are then studied.

Eleven parameters were varied in the Monte Carlo analysis of MAGIC in this study. These were the mean annual precipitation (QP). The cation exchange capacity (CEC), the weathering rates of each base cation (WECA, WEMG, WENA, WEK), the log selectivity coefficients (SALCA, SALMG, SALNA, SALK) and the equilibrium constant for the aluminium/hydrogen reaction (KAL). The Sulphate deposition loading was given the same shape as that compiled by the Warren Springs laboratory (1983) but was varied in magnitude by randomly selecting the 1981 level of deposition from a specified range of values. By varying KAL about the value for Gibbsite it was hoped to encompass a variety of aluminium reactions overlooked by the lumping of the model. The results of the Monte Carlo analysis were investigated using the Generalised sensitivity technique (Spear and Hornberger, 1980) This involves splitting the ensemble of runs into two groups: those that satisfy a predetermined behaviour criterion, and those that do not. The chosen behaviour criterion was to match the observed stream chemistry for 1981 to within 15%.

Kolmogorov-Smirnov and Mann-Whitney statistics were used to test the hypothesis that the parent distribution of parameter values that gives rise to a behaviour is the same as that for a non-behaviour. The hypothesis is rejected strongest by those parameters to which the occurence or not of a behaviour is most sensitive, thus the parameters may be ranked by their sensitivity. The Fukunaga-Koontz pattern recognition technique (Fukunaga and Koontz, 1970) is also employed in an attempt to discover any linear combination of parameters that show a high sensitivity. This entails finding the eigenvectors of the matrix that describes differences in the means and the variance-covariance for the two categories.

The group of runs that satisfied the behaviour criterion were used to deduce 95% confidence regions for each of the output variables throughout the time of simulation. These were obtained by fitting a distribution from the Johnson system of distributions (Johnson, 1949) to each variable at each time step. The Johnson distributions are based on a transformed normal variate and consists of three 4-parameter distributions. The method of matching quantiles was used to fit the empirical and theoretical distributions. (Slifker and Shapiro, 1980) The Kolmogorov-Smirnov test was performed to gauge the goodness of each fit.

APPLICATION TO DARGALL LANE

Dargall lane is a moorland catchment of Loch Dee. Situated in the Galloway hills of south west Scotland, it has a cool, wet climate with a mean annual rainfall of 2200mm. The altitude at the head of the catchment is 716m and the elevation falls to 225m at the lowest point. The soils are peaty podsols and peaty gleys with basin and valley peat in the lowest areas. Average soil depth in the catchment is 1 m. The soils are underlain by Silurian and Ordovician greywackes and shales with granitic intrusions dating from the old red sandstone age. Weekly sampling at Dargall Lane began in 1980. Chemical data is taken from Burns et al. (1984) who presented volume weighted annual average data for precipition and streamflow for 1981 (Table 1).

Background depostion levels (used to determine initial conditions in 1844) were calculated from the sea salt fraction of current deposition. Analysis of Dargall Lane chemistry reveals that the major components of precipitation chemistry are NA,CL and MG in concentration ratios similar to those in sea water. The K,Ca and SO_4 are assumed to be of terrestrial origin. Excess SO_4 correlates with the sum of H and NH4 indicating that sulphur compound emissions are the major cause in increasing rain acidity below pH 5.6. The most acidic episodes associate with winds from the south and south east where centres of high sulphur emissions are located.

Calibration of the model to the Dargall Lane catchment was performed by Cosby et al (1985a) and these results were used to set those parameters that were not varied in the Monte Carlo analysis. Future depostion was simulated as a linear decline to 30% of the present level by the year 2001. Results were saved every 10 years from 1844 to 2064. Table 2 shows the parameter ranges used for the Monte Carlo analysis. QP was assigned a triangular distribution with a peak at the mean observed level of 2.2m. The remaining parameters were given rectangular distributions which contained the values resulting from the previous calibration. The CEC was varied between 50 and 200 meq/kg, this compares with the 100meq/kg found by Bown et al (1982) for mineral horizons of peaty podsols and peaty gleys in south west Scotland. The behaviour criterion was chosen to match the 1981 concentrations, to within 15%, for CA,SO4,Mg,Na,CL and pH. Table 1 shows the simulated chemistry range for 1981 from those runs satisfying the behaviour criterion. The parameter values for these runs are summarised in table 2.

RESULTS

Of a total of 880 runs, 69 satisfied the Dargall Lane behaviour criterion. Figures 1 to 4 present the results for pH, Calcium, alkalinity and total aluminium. The model predicts that the alkalinity of Dargall Lane streamwater in 1981 is 80% of the pre-industrialisation level in 1844, of 45μeq/1. Calcium shows a rise of 40% from 37 to 52μeq/1 in the same period. The pH depression of 0.5 pH units agrees with the palaeoecoligical reconstruction of Flower and Battarbee (1983), although the simulated pH level is consistently about 0.5 units lower. The range of aluminium for 1981 is 1-9 μeq/1 with a mean of 2.5. This compares with an observed mean of 5.5 for the period 1982 to 1985 (Welsh et al., 1986).

TABLE 1 OBSERVED AND SIMULATED CHEMISTRY FOR DARGALL LANE

Variable	Observed		Simulated		
μeq/l	Rain	Stream	Mean	Min	Max
CA	16	52	48	45	53
MG	19	58	57	52	64
NA	83	137	132	123	151
K	6	12	11	8	16
SO4	48	79	82	74	87
NO3	19	19	17	15	19
CL	94	158	159	145	174
ALK	.	7	9	-11	22
pH	4.6	5.1	5.4	5.1	5.6
%BS		5-10	7.5	4.5	10.2

(ALK is alkalinity and %BS is the percentage base saturation of the soil)

TABLE 2 PARAMETER RANGES USED FOR MONTE CARLO ANALYSIS OF DARGALL LANE.

	Monte Carlo ranges		successful simulations			
Parameter	minimum	maximum	mean	var	min	max
QP m.	1.5	3.	2.0	.23	1.5	2.9
SO4 meq/m2/yr	50	70	58.8	6.0	52.7	62.1
CEC meq/kg	50	200	168	221	56.1	197.4
WECA meq/m2/yr	20	100	37.3	93.8	16.3	66.5
WENA " "	0	50	11.7	71.3	.3	30.5
WEMG " "	0	50	7.8	35.6	.3	24.9
WEK " "	0	20	3.0	5.4	.1	18.2
SALCA	-1	5	1.96	2.02	-.7	4.7
SALMG	-1	5	1.93	1.67	-.5	4.6
SALNA	-3	3	.00	1.59	-2.6	2.3
SALNA	-3	3	-.24	1.73	-2.7	2.4
KAL	8	11	9.70	.63	8.4	10.9

The overall trend is for a decrease in pH, alkalinity and base saturation and an increase in base cation and aluminium concentrations with increasing deposition. The base saturation of the soil declined from a mean of 10.2% in 1844 to a mean of 7.5% in 1981, revealing a depletion of base cation resource in time. The range of possible base saturation values increased steadily through time and was 4.5-10.2% in 1981. The fall in pH and alkalinity slows down between 1965 and 1980 whilst the deposition levels drop. A small recovery of .1 pH unit and 6μeq/l alkalinity results from the ramped decline to 30% of 1981 deposition levels by 2001, in the future deposition scenario. The ramp induces an overshooting of the final equilibrium levels, leaving the model to gradually attain equilibrium from 2001. The 95% confidence regions for model simulations show small variation through time for pH (.3 to .5 pH unit) and for alkalinity (28 to 42 μeq/l), whereas for calcium the range narrows (20 to 10 μeq/l) and for aluminium the range broadens (0-9μeq/l) through time. The range of possible pH value is similar in size to the error band presented in the palaeoecology results. The aluminium starts to be released when the pH level drops below 5.5. The amount released reaches a peak at the same time as the pH reaches its minimum of 5.38 in minimum of 5.38 in 1975. Calcium response is more immediate then that of pH since the pH levels are buffered by the base cations on the soil matrix and by sulphate adsorption in the soils. The calcium levels therefore reach their peak in 1961, before the pH finds its minimum.

The Kolmogorov-Smirnov tests of the fitted Johnson distributions revealed only two supect fits at the 80% level of confidence: total aluminium in 1921; and alkalinity in 1941. These are not included in the graphs.

APPLICATION TO ROUND LOCH OF GLENHEAD

The Round Loch of Glenhead is sited on the granitic intrusions in the Galloway hills, with an overall geology similar to that of the nearby Dargall Lane and a soil type mainly of blanket peat of .75m depth. The area of the loch is 12.6 hectares and the altitude is 295 m. The catchment is a non forested one with diatom evidence of strong acidification during the past 130 years (Battarbee and Flower, 1985).

The mean temperature of the loch is 9 C and the mean annual rainfall is 2.2 metres. The mean annual pH of the loch is low at 4.7 as is the calcium level of 30 μeq/l for 1984 (Flower Rippey and Tervet, 1985). The main chemical features of the loch are otherwise similar to Dargall Lane. Table 3 shows the data for 1984 stream quality levels (from Harriman et al., 1986). The model was set up as previously described for Dargall Lane. The parameter ranges used for the Monte Carlo analysis are presented in table 4. The results of the simulations and the parameters that gave rise to the successful simulations are shown in tables 3 and 4.

RESULTS

Out of 880 runs, 124 satisfied the behaviour criterion. The trends for The Round Loch are shown in figures 5 to 8. Here there is a sharp decline in both pH and alkalinity during the years 1844 to 1984 amounting to twice that seen for Dargall Lane. Simulated aluminium levels in 1984 are higher than those reported by Flower, Rippey and Tervet (1985) of 25μeq/l and Harriman et al (1986) of 13.9μeq/l. The pH decline of 1 pH unit is in excellent accord with the palaeoecological reconstruction of Battarbee et al (1985), as is the confidence range of almost .4 of a pH unit (figure 9). The same overall trends are seen for Round loch as were seen for Dargall Lane both in terms of the mean response to deposition and the range of possible responses. The converging calcium range reflects the nonlinear increase in difficulty of extraction of the finite cation resource through exchange. Thus as the base saturation decreases so does Eca in the Gaines Thomas expressions of equation 4. The mean base saturation falls from 8.5% in 1844 to 3.5% with a range of 2-5 % in 1984. It is this very low base cation resource that enables the pH to fall to 4.7. No recovery in base saturation is seen by 2061 under the future deposition, although the depletion rate slows down considerably.

The test of the Johnson distribution fits once again revealed only two suspects: alkalinity in 1901, and total aluminium in 1921. These are not included in the graphs presented.

TABLE 3 OBSERVED AND SIMULATED CHEMISTRY FOR ROUND LOCH OF GLENHEAD

variable (μeq/l)	Observed stream	Simulated mean	min	max
CA	30	28.5	24	32
MG	41	41.	37.2	48.4
NA	113	118	105	124
K	10	9.2	5.3	13.1
SO4	111	112	100	121
NO3	6	7.2	4	9.3
CL	136	139.5	125	149
ALK	.	-52	-74	-28
pH	4.65	4.7	4.6	4.8
BS	.	3.2	1.8	5.0

TABLE 4 PARAMETER RANGES FOR ROUND LOCH

parameter	Monte Carlo ranges min	max	successful simulations mean	var	min	max
QP m.	1.5	3	2.15	.15	1.51	2.9
SO4 meq m-2yr-1	60	120	93.6	23.7	85.1	101.3
CEC meq/kg	40	150	86.5	121.5	41.3	148.7
WECA meq m-2yr-1	0	100	11.9	45.7	2.3	32.7
WEMG " "	0	50	12.5	29.6	.2	28.2
WENA " "	0	50	4.2	12.1	.4	9.7
WEK " "	0	30	7.1	16.0	.3	13.6
SALCA	-1	5	1.90	1.3	-.2	4.3
SALMG	-1	5	1.98	1.45	-1.7	4.7
SALNA	-3	3	-.10	1.41	-2.7	2.2
SALK	-3	3	-.00	1.49	-2.5	2.4
KAL	8	11	9.6	.72	8.2	10.7

SENSITIVITY OF PARAMETERS

The generalised sensitivity analysis was performed from the results for the Round loch simulations. The results are shown in table 5.

TABLE 5 SENSITIVITIES OF BEHAVIOUR TO PARAMETERS

comparison of behaviours to non-behaviours

parameter	Mann-Whitney z statistic	Kolmogorov-Smirnov d statistic
QP	8.86	.443
SO4	3.19	.168
CEC	4.94	.219
WECA	7.42	.365
WEMG	1.42	.108
WENA	.97	.067
WEK	1.29	.097
SALCA	1.40	.095
SALNA	1.08	.109
SALK	1.03	.048
KAL	.64	.052

The most sensitive parameters are seen to be the precipitation volume QP and the weathering rate of calcium WECA. Of less significance are the 1984 sulphate deposition levels, SO4 and the cation exchange capacity CEC. The effects of the QP and the weathering rates are cumulative through time in the model QP and this might partly explain their sensitivity ranking. The calcium weathering rate is very significant to the calcium levels in the stream when they are low, as in the case of the Round Loch. In such cases when the cation content of the soil is low the calcium can pass through to the stream straight from weathering thus "bypassing" the soil exchange mechanism. The eigenvector analysis revealed no combinations of parameters that outstripped QP or WECA in sensitivity. The most significant eigenvector had a Mann-Whitney U-statistic of -5,79 and a Kolmogorov-Smirnov d statistic of .263. The weights of each parameter in the normalised eigenvector reflect the importance of that parameter within the vector. The largest component of the most sensitive vector was QP, which accounted for 43% of the information contained by the vector. Next was SALCA with 15%. Thus the soil parameters for calcium and the rainfall are perceived to be most influential in producing a successful simulation for the Round Loch. A look at the relative positions of the probability density functions for behaviours and for non behaviours showed some overlap between the two for all parameters. This indicates that no parameter independently controls the occurence or not of a behaviour. If this were the case then the density functions would show a region of parameter space which precludes the existence of either the behaviours or the non behaviours. This analysis suggests the combination of parameters ultimately controlling the outcome to be non linear.

DISCUSSION

Uncertainty in the MAGIC model resides in its structure, the deposition sequence used and the parameter set chosen to represent a given catchment.

These uncertainties may propagate through to uncertaity in the model state in simulated time. The evaluation of uncertainty in model structure is difficult for a complex, non linear model such as MAGIC, although a sensitivity analysis of the model output to the soil processes represented by the model is possible (COSBY et al., 1986c). Work may proceed under the assumption that the structure is correct, enabling the remaining uncertainties to be investigated (e.g. HORNBERGER et al., 1986) For the MAGIC model two considerable problems remain to be those of calibration and verification. For long term simulation models of environmental systems there is a lack of data sufficient for rigorous calibration. Short term data abounds and can be used in conjunction with palaeoecoligical reconstructions of pH to provide a mixed term constraint on catchment behaviour for model calibration. This method has produced some good agreement between simulated and observed chemistry for a MAGIC in a variety of catchments in Scotland, Sweden, Norway and the U.S (Wright et al., 1986). The problem of selecting a "correct" set of parameters for each application is impossible to solve without detailed information on soil, soilwater and streamwater characteristics in both time and space. This sort of data is rarely, if ever, collected. Even with this data there is a problem with assessing the values that the lumped parameters must take, given their heterogeneous counterparts. The "true" set of parameters may be bounded by randomly sampling from a parameter set that encompasses the spectrum of known possible spatial values, and by filtering the given model through a behaviour criterion. In this way all combinations of parameters that produce a good fit to the observed data can be utilised to present boundaries for the values of the response variables. This allows regions to be found within which the solution must lie if the model and the deposition sequence is valid for the catchment. Though the uncertainty in the deposition sequence is not known, the sensitivity of the model to changes in the sequence can be found (Hornberger at al., 1986). Uncertainty in the deposition sequence is less important for catchments with a fast response time (of the order of a year or less), such as the Dargall Lane and the Round Loch of Glenhead. These soils in these catchments are mainly peat and do not adsorb much sulphate. The bedrock is hard and slow to weather, ensuring low buffering capacity and quick response to deposition. The behaviour criterion selected may also incorporate uncertainty through measurement error. This has been compensated for in this analysis by allowing 15% leeway on the observed chemistry used for the behaviour windows. The resulting range of accepted response is therefore wider than if a narrower behaviour filter were used.

CONCLUSIONS

The long term chemistry of two catchments in an area of south west Scotland with high susceptibility to acidic deposition has been simulated. A lumped parameter model was used that modelled five soil processes believed to be important in effecting the changes in the soil arising from acid deposition. This model enabled an historical reconstruction of pH that closely resembled those obtained for the same catchments via diatomic studies. Bounds on the model prediction were able to be placed using Monte Carlo methods. The rate of acidification through time was simulated and the recovery of the catchment under assumed future deposition scenarios may be seen. It is suggested that recovery is slow for the two catchments simulated.

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Figure 1 DARGALL LANE SIMULATION

pH

(mean and 95% confidence levels)

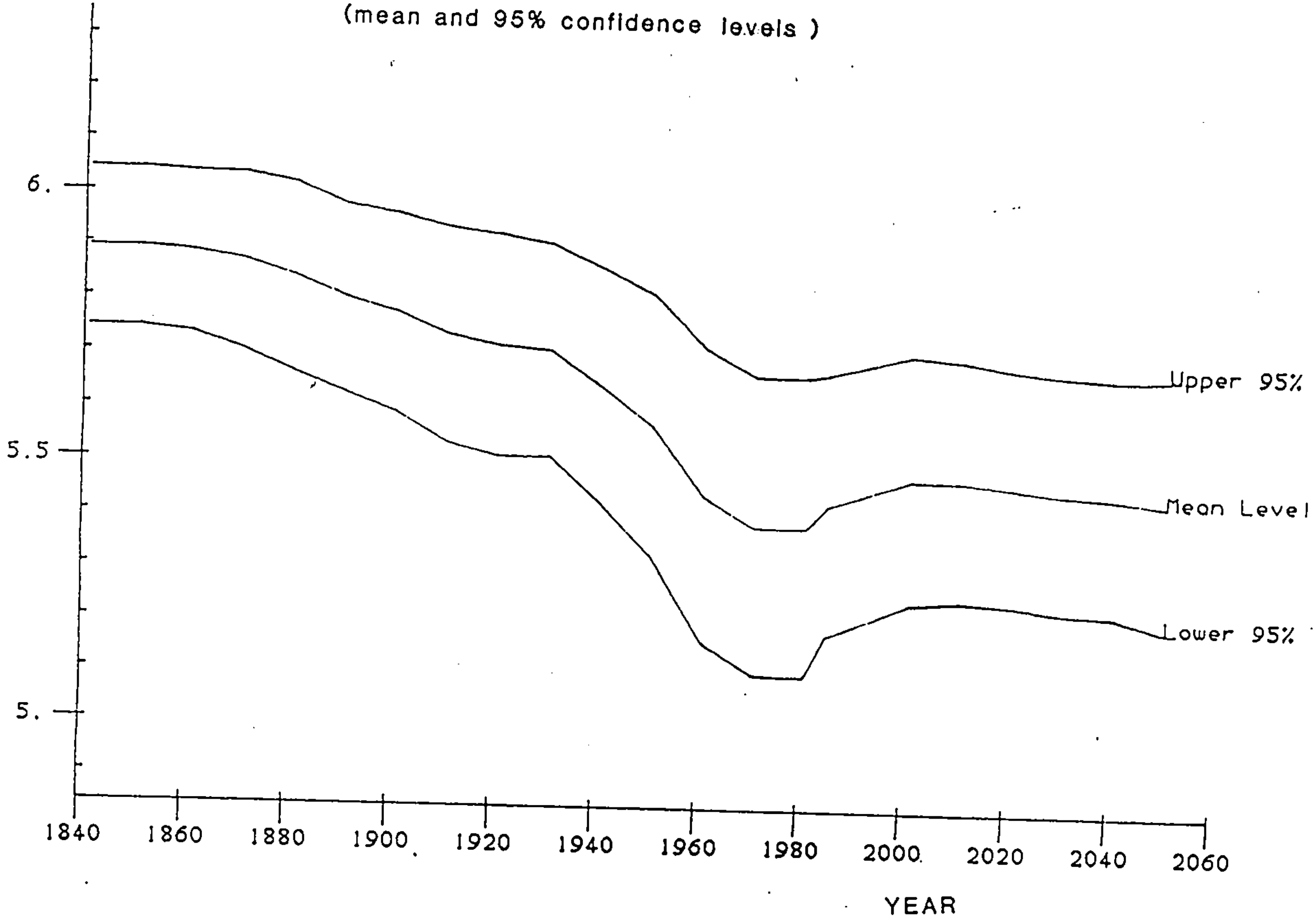


Figure 2 DARGALL LANE SIMULATION

CALCIUM

(mean and 95% confidence levels)

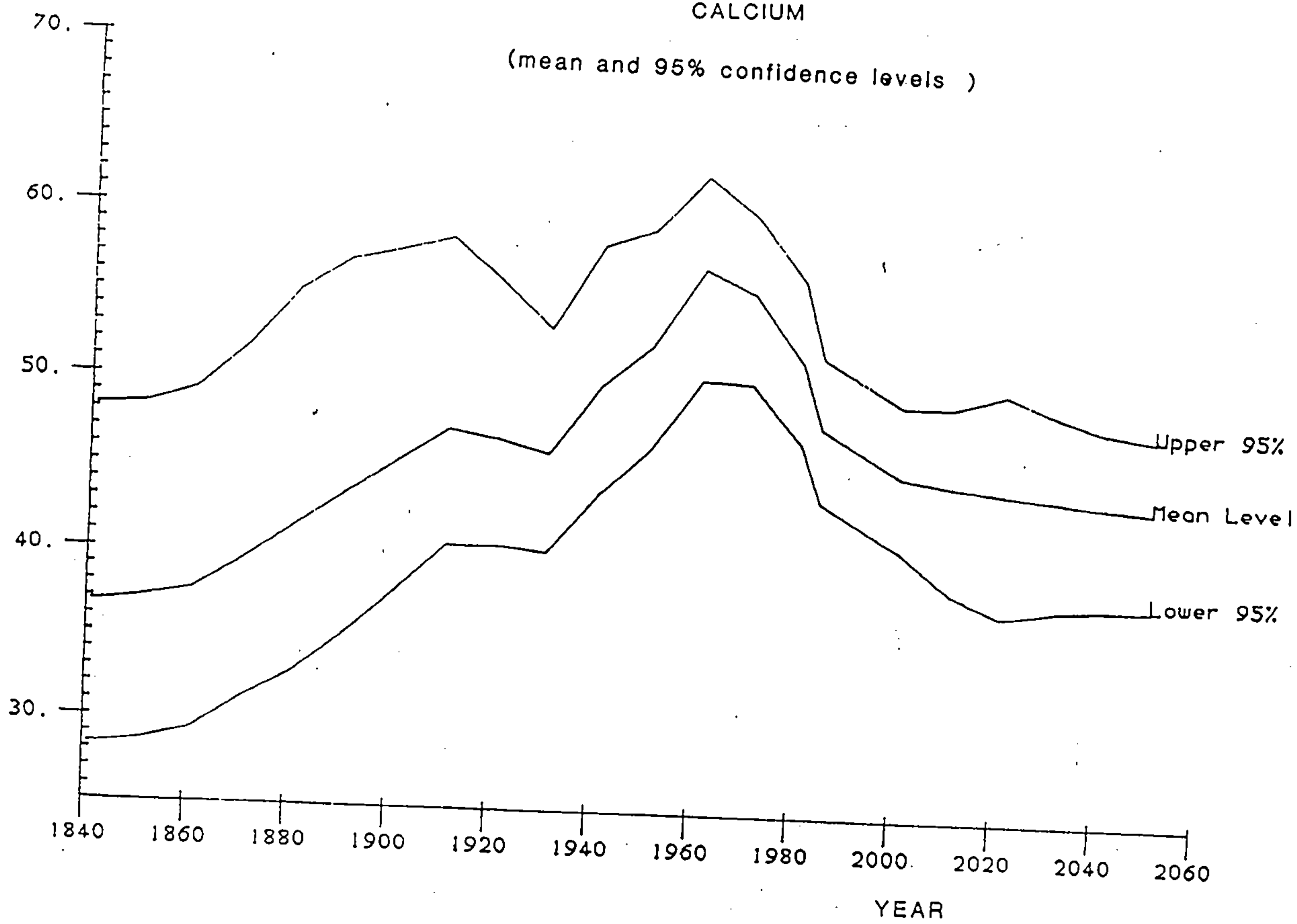


Figure 3 DARGALL LANE SIMULATION

ALKALINITY

(mean and 95% confidence levels)

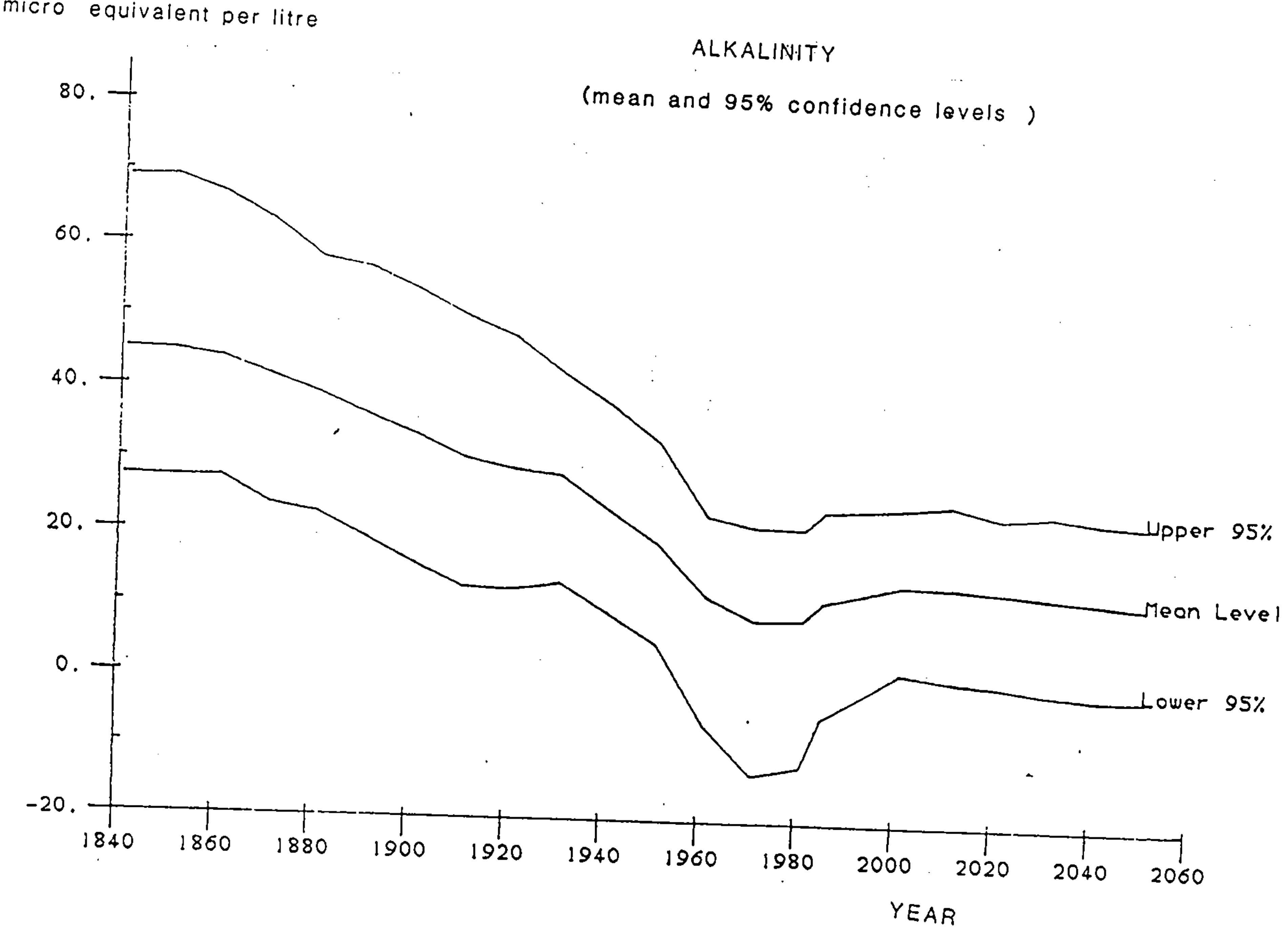
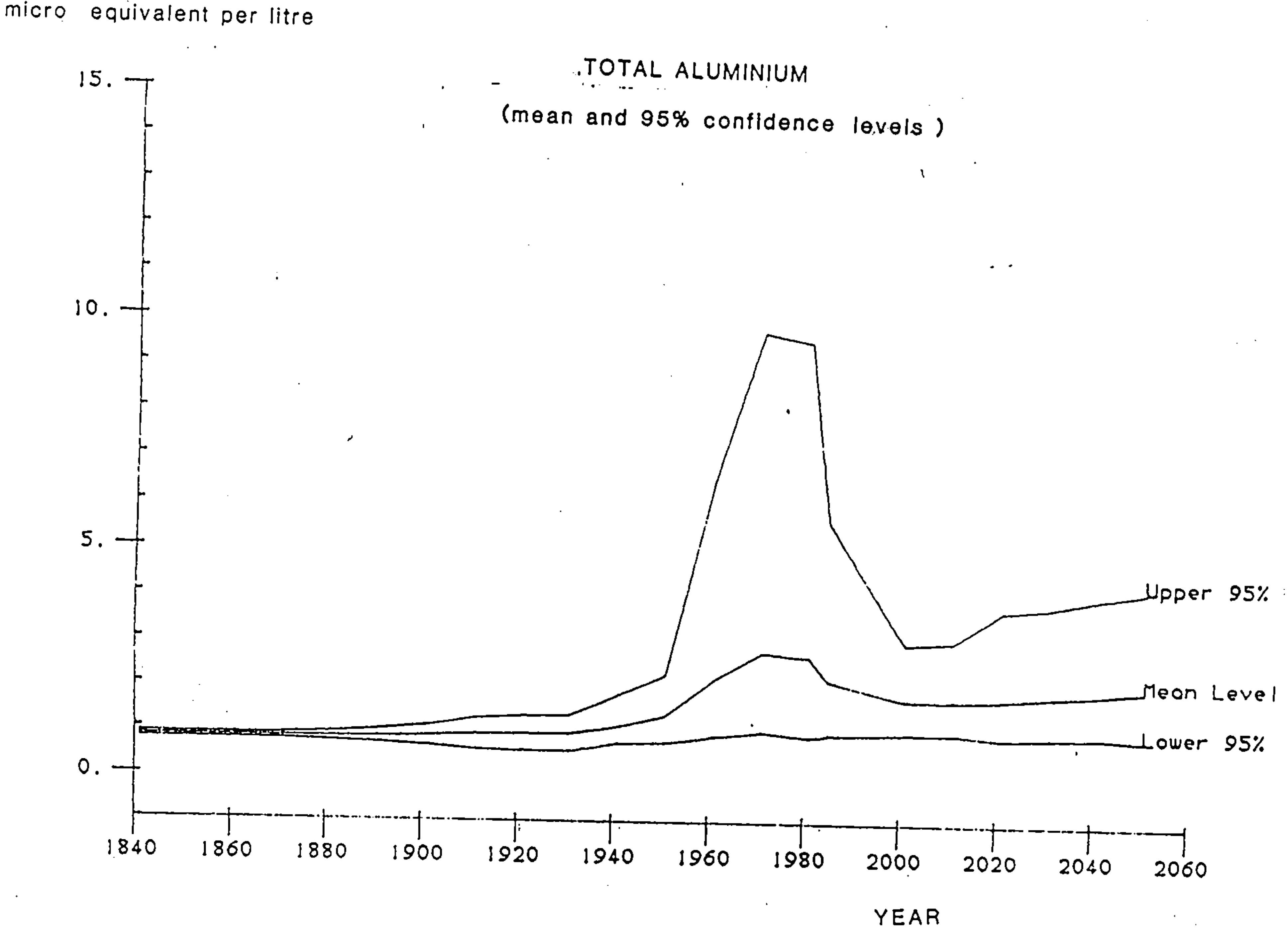


figure 4 DARGALL LANE SIMULATION



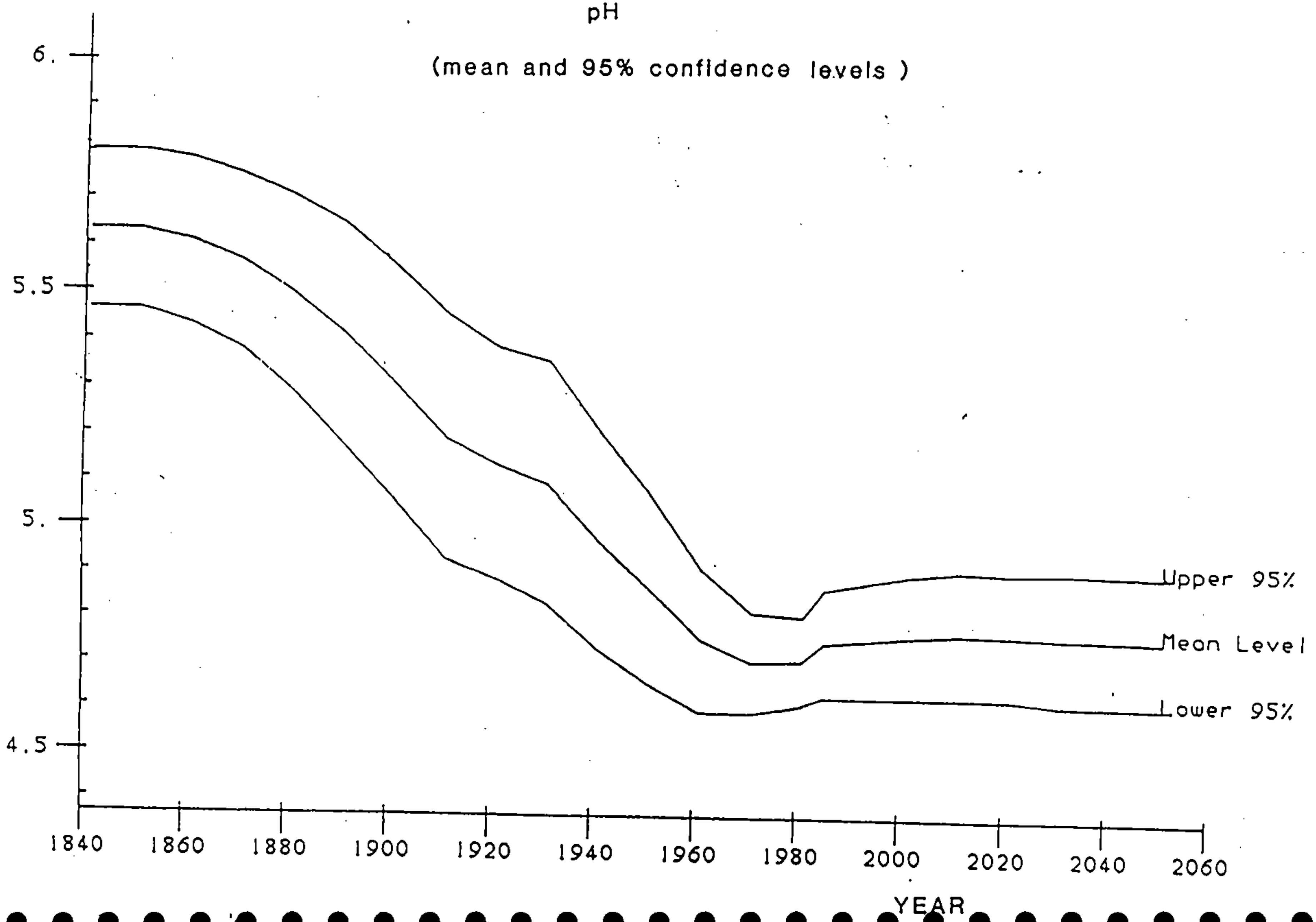


Figure 5 ROUND LOCH OF GLENHEAD SIMULATION

pH

(mean and 95% confidence levels)

Figure 6 ROUND LOCH OF GLENHEAD SIMULATION

CALCIUM

(mean and 95% confidence levels)

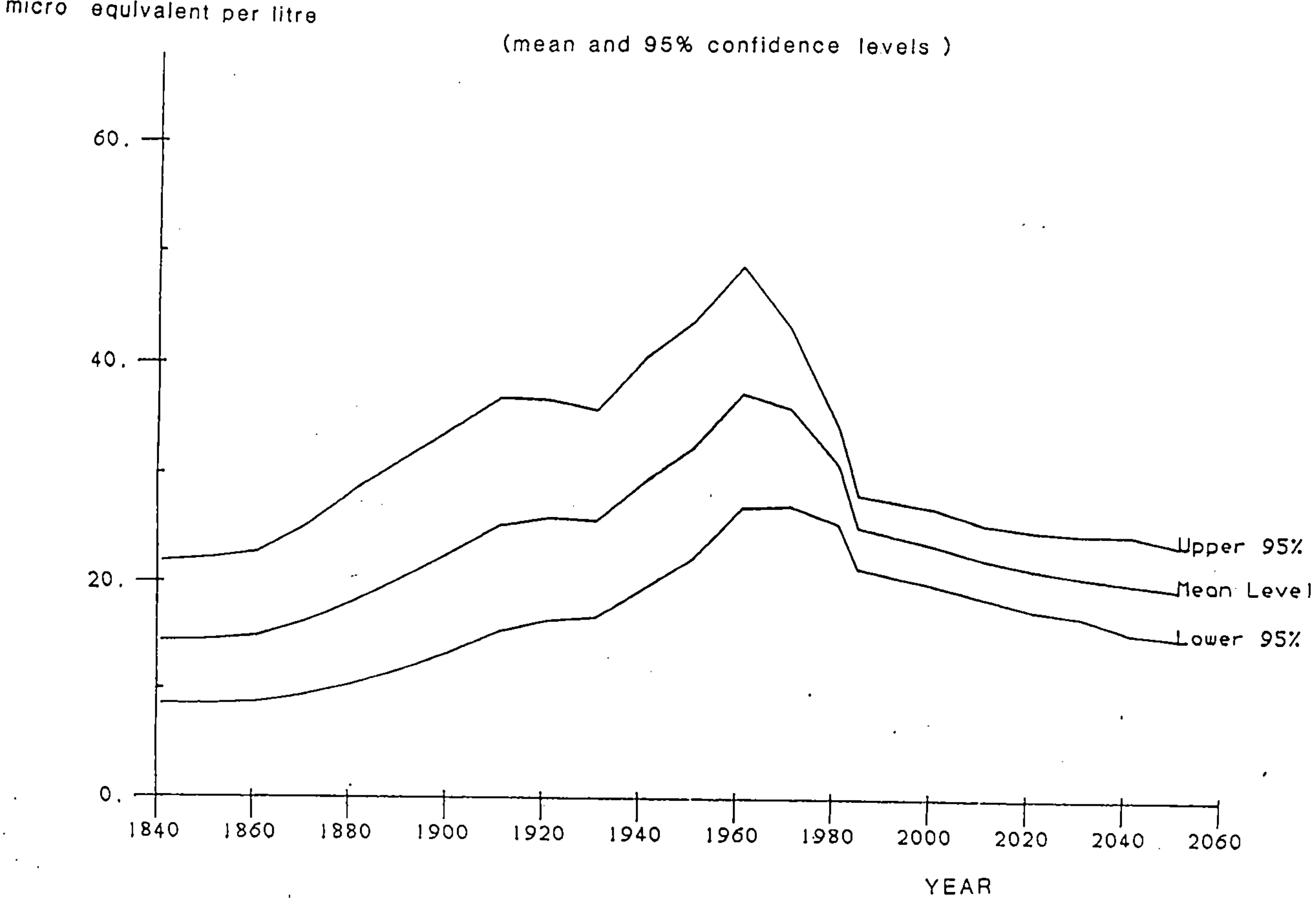


Figure 7 ROUND LOCH OF GLENHEAD SIMULATION

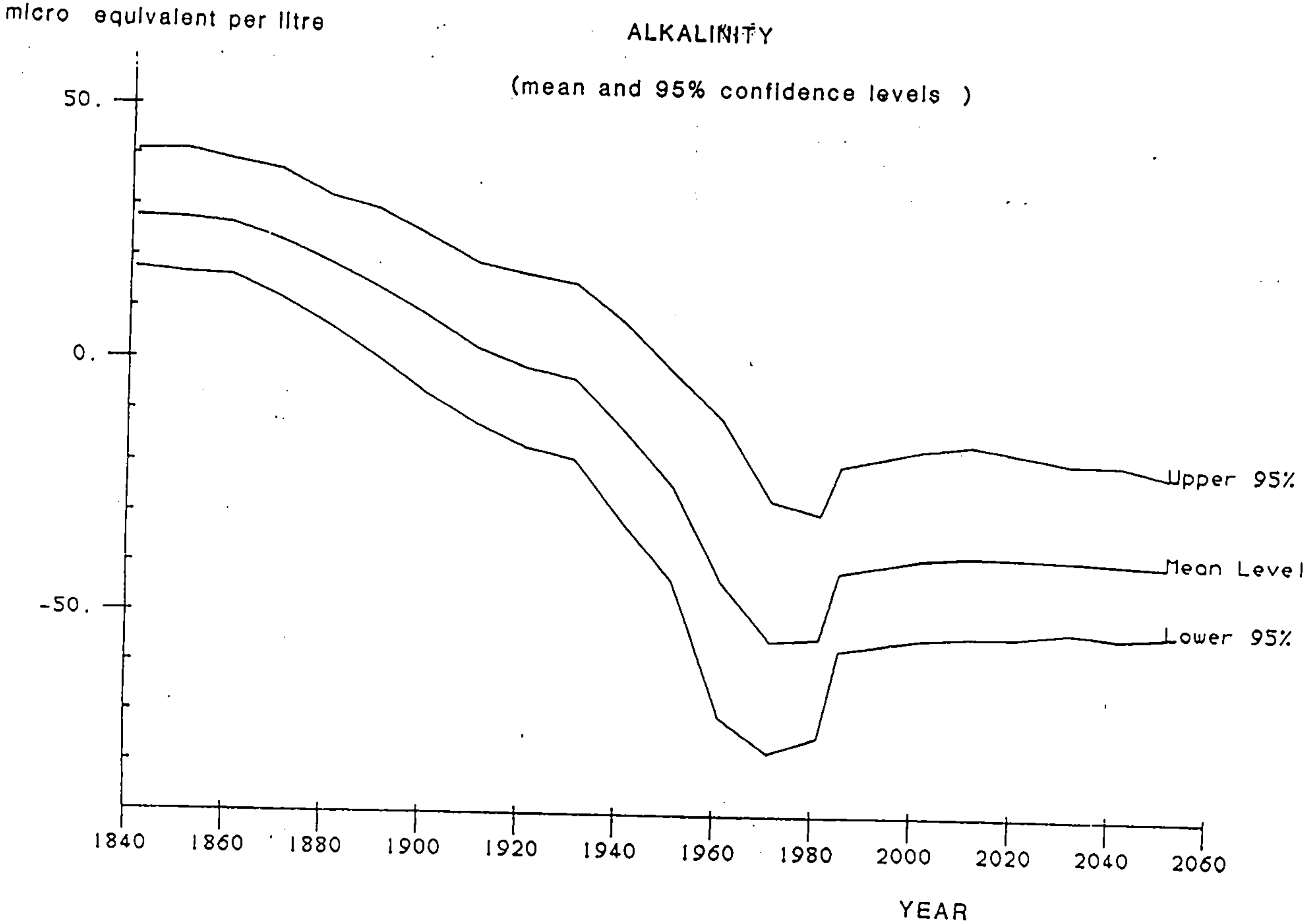
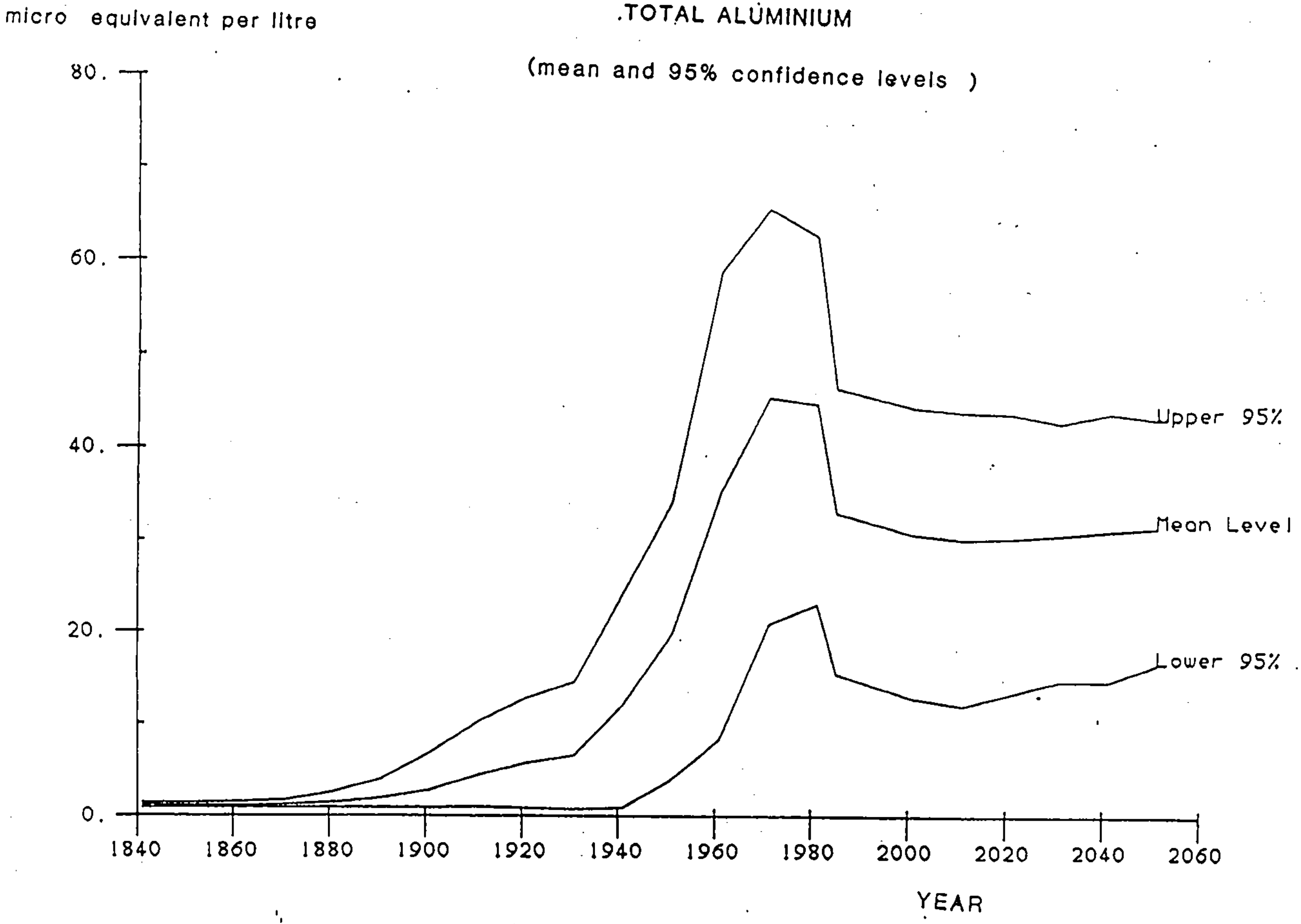


Figure 8 ROUND LOCH OF GLENHEAD SIMULATION

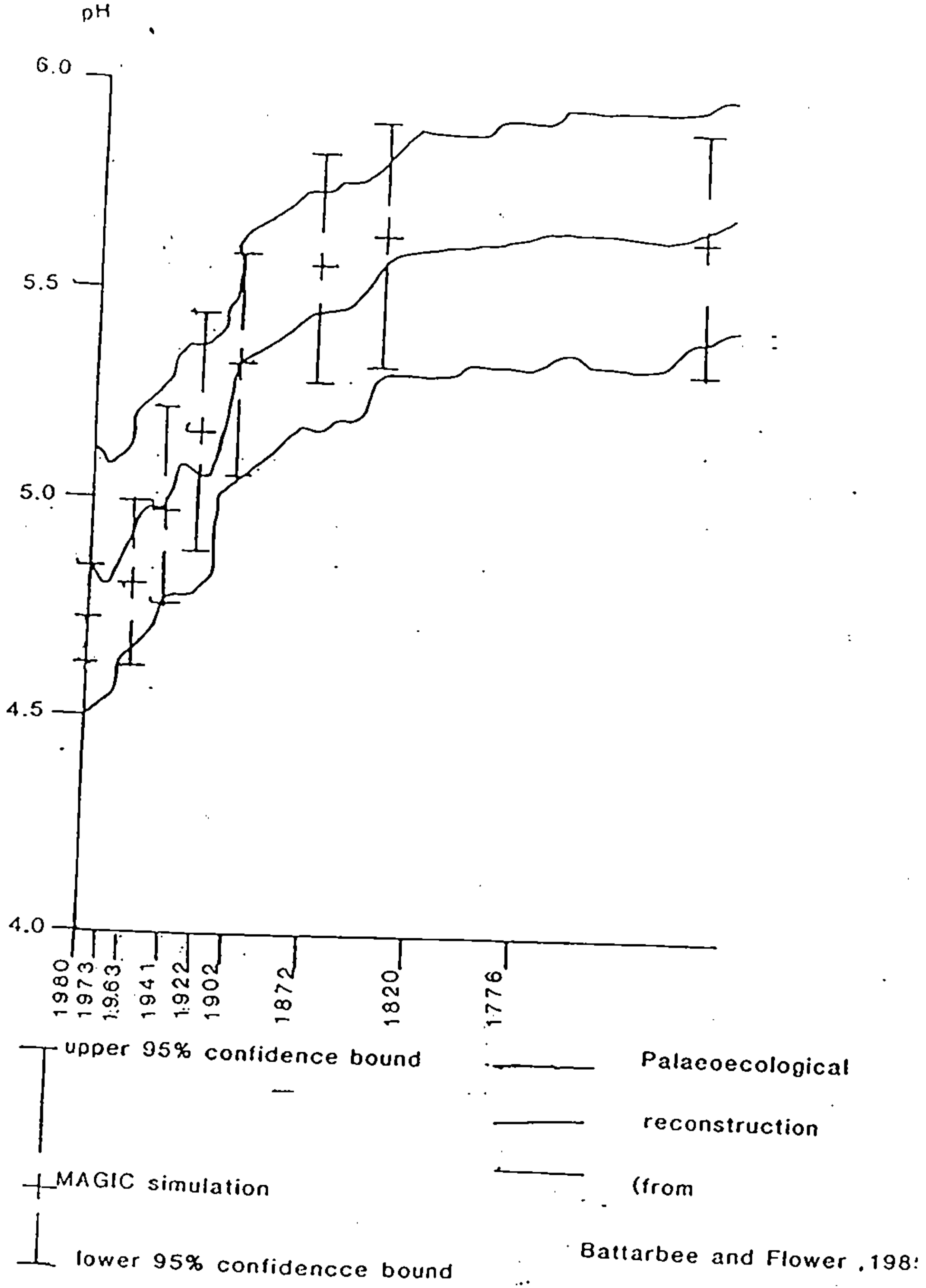


.TOTAL ALUMINIUM

(mean and 95% confidence levels)

Figure 9 ROUND LOCH OF GLENHEAD SIMULATION

COMPARISON WITH PALAEOECOLOGICAL RESULTS



APPENDIX 2

REGIONAL modelling of acidity in the galloway region in south west scotland

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ABSTRACT

Regional scale surface water characteristics of the Galloway area of south west Scotland are simulated using the MAGIC model of acidification of groundwater in catchments . Data from several studies within the area are pooled to provide a large , single data set for calibrating the model. The Monte Carlo technique is employed with the MAGIC model to produce a wide ranging model response encompassing the observed chemical features of the region. The simulation indicates that a substantial portion of the Galloway area has been significantly acidified during the past 140 years.

INTRODUCTION

The south west region of Scotland is believed to be particularly vulnerable to the effects of acidic deposition, Wright and Henrikson (1979). Reports of long term changes in acidic status of lakes and streams combine with reports of a decline in fish populations to present a picture of concern to freshwater fisheries and environmentalists alike (Battarbee and Flower ,1986, Burns et al. ,1984). Action to reverse the observed trends can only be effectively prescribed once the processes within the catchment soils that transform acidic precipitation into stream water pollution are understood. Practical experimentation in the laboratory and in the field can help to explain part of the story. The picture for soils, however,is obscured in the field by their heterogeneous nature, and in the laboratory by the inability to exactly reproduce field conditions. Mathematical models are very useful as an aid to undestanding the intrinsic processes in complex systems such as the soil- water chemical interaction through time and space. By using models, hypotheses may be tested by simulating processes and the results compared to their measured counterparts . Useful information may often be deduced irrespective of the outcome of the comparison.

In this study we use a well documented and extensively used model of groundwater in catchments (the MAGIC model) to perform a regional analysis of lakes and streams in south west Scotland. Instead of modelling each lake and stream separately we pool them all and model their overall probability density functions of water chemistry variables. We use the Monte Carlo technique to run the model many times,taking for each run a different set of parameters randomly sampled from specified distributions. The runs that enable us to match the observed distributions are investigated to determine the sensitivity of the model results to the individual parameters . The changes that have occured in the region as a result of increased deposition during the past 140 years are simulated and a possible future scenario of deposition is enacted.

ANALYSIS OF CHEMICAL DATA FOR THE GALLOWAY REGION

The Galloway Region of South West Scotland contains many lochs and streams that drain moorland,, forest and pasture catchments. The bedrock consists mainly of lower palaeozoic rocks of Ordovician and Silurian systems with a few intrusions of Granite of the Old Red Sandstone era (Harriman et al.,1986). These catchments have only a thin covering of unconsolidated glacial till, often closely related to the nature of the underlying rocks (Greig,1971). Many catchments in the region are covered by a blanket layer of peat of between 50 and 100 cm thickness. The southern part of the region is reported to have a higher calcite availability than the northern part. (Welsh et al. ,1986 , Edmunds and Kinniburgh,1986). The mean yearly rainfall ranges from .8 to 2.4metres with a mean of 2.0 metres. The concentrations of the major ions indicate three important sources: terrestrial input of Ca,Mg,Al,HCO_3 as products of weathering; atmospheric pollution input of H,NH_4,NO_3 and SO_4; and atmospheric input of seawater salts Na,Cl,Mg and SO_4 (Wright et al.,1980). The distribution of these ions varies spatially with a regional character. Concentration of all the major ions is higher nearer the coast to the south. Pollutant concentrations are higher as a result of the location of the sulphur emission areas to the south and the south east of Galloway. Weathering is highest in the more calcareous Silurian and Ordovician rocks to the south rather than the slowly weathering harder Granitic intrusions to the North. Sea salts are more evident nearer the coast. The pH of precipitation is 4.1 to 4.4 and contains a large excess sulphate proportion (Wright and Henrikson,1979). The region as a whole is believed to be highly sensitive to acidic deposition and is therefore a useful area for scientific study .

Data sets from four separate investigations in Galloway were used in the study.Firstly, Edmunds and Kinniburgh(1986) sampled sites during the wet summer of 1985 as part of a larger survey of groundwaters throughout the United Kingdom. They took spot samples from springs, shallow wells, boreholes and river baseflow from a 20 km by 25km area extending from Wigtown in the south to Loch Macaterick in the north and from the River Luce to the east to the Waters of Ken to the west. The study encountered the full range of Galloway bedrock but sampled few coastal sites. Secondly, Wright and Henrikson (1979) took spot samples from 72 lochs and 39 streams during the wet period in 19-26 April,1979. The data was compared to an area of similar acidic susceptibility in Norway. The area of study was 70 km by 50 km and covered the entire Galloway region.These samples thus enveloped the complete spectrum of Galloway chemistry. Thirdly, Flower et al.(1987) looked at the water quality and diatom content of 34 Galloway lochs in November 1984 and again in July 1985. The study area once again encompassed the whole of Galloway. Finally, Harriman et al.(1986) sampled 22 lochs and 27 streams, looking at their chemistry and their fish populations. The region of study was limited mainly to the Granitic area between loch Dee and loch Doon in a 20km by 15km area.

A summary of each data set is presented in table 1. It is seen that the highest mean pH levels were recorded by Flower et al., in their July sample and by Edmunds and Kinniburgh , for whom the shallow well and borehole samples show the more alkaline groundwater chemistry. The latter study also shows the highest base cation concentrations. The data from Harriman et al. shows the low chemical concentration indicative of the slowly weathering , acidic Granite region away from the coast and the emission sources. Of the major anions, SO4 levels are more or less similar at approximately 158 meq/m3 , but Cl is more variable ranging from 148 to 385 meq/m3.

The probality density distributions of corresponding chemicals within data sets are roughly triangular with a tail of varying length. The tail values affect the mean results in table 1 by shifting them from their respective median values. This effect is greatest for the three data sets with a low number of samples. The distribution of pH has three peaks, at 4.5, 6.1 and 7.1, for each of the studies except for that of Harriman et al., who sample the most acidic area and hence only show the lower two.

The data were pooled together to yield a large data set whose samples covered a variety of conditions produced by both spatial and temporal variation within the region. The samples were all taken within a five year period, and it was assumed that the pooled set could represent the mean state of the region during those five years. The time scale of the model is large compared to this and the errors introduced by such an approach were considered to be outweighed by the benefit of utilising all of the data to get a more accurate representation of region as a whole during that time. The overall mean results are presented in table 1. Probability density functions showing the three peaked pH distribution and the long tailed "triangular" distribution for Calcium, but also typical of each of the major ions, are shown in figures 1 and 2.

A cluster analysis was performed on the data in an attempt to categorize groups of data linked by a common chemical make up. The minimum variance method of Ward was used to cluster the data (Ward ,1963) and the algorithms used were those available in the Statistical Analysis Systems computer package (SAS user guide, 1983). The clearest division of the data was obtained by forming six clusters. Two main clusters contained 322 and 74 of the total sample of 453 sets of measurements , and four minor clusters effectively accounted for the long tails of the distributions for the appropriate chemicals. Table 2 shows summaries of the two major clusters. Cluster 1 has a mean pH of 5.3 and includes all the low pH sites. Concentration of all major ions is low, e.g. mean Ca is 83 meq/m^3 and mean SO4 is 120 meq/m^3. This is contrasted by Cluster 2 which has high values for ions (Ca is 412 meq/m^3 and SO_4 is 216 meq/m^3, see figures 3 and 4), with a mean pH of 6.4. The differences may be interpreted by assuming that cluster 1 contains the more acidic sites on and around the Granitic regions to the north of the Galloway region, and that cluster 2 represents the area with Silurian and Ordovician bedrock near to the coast. Cluster 2 chemistry thus reveals the prevalance of higher deposition rate of sea salt and of atmospheric pollutant and also the higher source of weathered minerals. The main interest focuses upon cluster 1 as representing the most acid sensitive subdivision, and here only the simulation for cluster 1 is presented .

TABLE 1 A SUMMARY OF DATA FROM EACH STUDY
(MINIMUM,MEAN,STANDARD DEVIATION,MAXIMUM)

all meq/m³ except Al(mg/l)

Data set		pH	Al	Na	K	Ca	Mg	Cl	SO4	NO3
Kinniburgh & Edmunds	min	4.2	.01	96	0.	19	16.5	28.2	37.5	0.
	mean	5.8	.21	277	26.7	329	158	253	159	49.5
	std	.85	.21	153	65.3	38.7	171	192	112	125.5
	max	7.3	.8	1095	644	2136	1242	1291	1041	728
Wright & Henrikson	min	4.3	.01	101	1	6	21	37	47	0.
	mean	5.4	.19	210	19.8	174.5	107	233	163.8	35.5
	std	.92	.18	113	16.1	300	95	143	77	65
	max	7.6	1.1	761	176	1811	403	930	478	460
Harriman et al.	min	4.2	.01	100	3	15	34	100	88	1
	mean	5.2	.17	143	9	139	78	148.6	150.5	11.3
	std	.6	.1	29	2.3	92	31	32	36	6.6
	max	8.0	.62	257	13	1325	429	232	279	45
Flower et al. nov 84	min	4.4	.1	1748	4.6	14	38	90	54	.7
	mean	5.5	.21	286	13.4	134	121	385	161.5	17
	std	.9	.11	138	12	114	83	179	85	31
	max	7.0	.43	765	56.3	400	340	935	358	171
Flower et al. jul 85	min	4.5	.07	135	3.1	23	37	87	70.8	.7
	mean	6.0	.27	276	14.7	166.3	116	298	139	7.5
	std	1.3	.4	164	14.6	142	88	163	67	7.2
	max	7.2	.59	717	64	518	356	899	320.6	31.4
overall	mean	5.65	.21	248	21.5	248.6	132	250.4	158	37

TABLE 2 SUMMARY OF THE TWO MAJOR CLUSTERS

Variable	number	mean	standard deviation	minumum	maximum
CLUSTER 1	:				
Al	322	.312	.16	.01	1.05
Ca	322	82.9	52.9	6.0	339.3
Cl	322	189.8	80.1	28.2	541.5
SO4	322	120.3	42.7	37.4	341.5
pH	322	5.34	.79	4.18	7.38
NO3	322	8.75	13.3	3.57	89.0
Mg	322	69.0	31.7	16.5	310.2
Na	322	184.7	60.2	1.0	404.3
K	322	8.6	11.4	2.6	130.5

CLUSTER 2:

Al	74	.172	.11	.01	.42
Ca	74	412.1	120.0	196.1	748.5
Cl	74	332.2	135.5	87.4	631.7
SO4	74	216.5	80.9	99.9	449.7
pH	74	6.4	.56	5.38	7.44
NO3	74	54.8	57.8	3.57	298.4
Mg	74	204.9	73.1	90.5	477.2
Na	74	361.3	110.2	169.6	776.1
K	74	31.6	30.4	2.5	181.6

DESCRIPTION OF MODELLING TECHNIQUES

The region was modelled using the Model of Acidification In Catchments(MAGIC), developed by Cosby et al.(1985a and b). This is a lumped parameter long term simulation model of soil and surface water quality. In the MAGIC model, five soil processes are identified as holding the key to understanding the acidification processes in soils. These are: formation of alkalinity in the soil from dissolution of carbon dioxide held at high partial pressure (Reuss and Johnson,1985); mineral weathering of base cations as a source within the catchment; anion retention by the soil,e.g. sulphate adsorption; aluminium mobilisation and dissolution of aluminium minerals; and cation exchange by the soils. Dynamic variation in the catchment soil condition is included in the model by forming a mass balance for each of the major anions and cations (presented by Cosby et al. 1985b). Equilibrium is assumed for each time step with changes between time steps monitored by the ion flux budgets. The sulphate subsection of the model is investigated in detail by Cosby et al.(1986b). Initial conditions for the model are calculated by assuming an equilibrium with background chemistry prior to industrialisation in 1844. Deposition of the major ions is specified as an input to the model. The trend of Sulphate deposition during the past 140 years is taken from findings of the Warren Springs laboratory in 1983. The effect of catchment flora is modelled as sink terms for the appropriate ions. Neal et al.(1986) and Whitehead et al.(1987) use this facility to simulate the effect of forest growth on stream acidity. The model has a simple component for the additional effect of organic chemistry,which has been applied by Lepisto et al.(1987) to simulate an organically rich catchment in eastern Finland. An analysis of the uncertainties inherent in the model is proffered by Hornberger et al.(1986),whereas Musgrove et al.(1987) investigate the precision of the simulation results. Verification of the model has been attempted by comparing model simulations to palaeoecoligical reconstructions of pH for sites in Norway, Scotland, Sweden and America (Wright et al.,1986). The use of the model for regional analysis is illustrated by the study of Cosby et al.(1987), who simulate the regional characteristics of the chemistry of 208 lakes in Norway.

For this study the model was set up for Monte Carlo analysis. In this technique, several arbitrary parameters are randomly selected from a prescribed parent distribution prior to running the model. This is repeated many times in order to build up a set of runs, each with a different set of parameter values. The statistical properties of the collection of runs are then analysed. Examples of this technique applied to water quality problems are presented in Whitehead and Young(1979),Spear and Hornberger (1980a and b) and Spear and Hornberger (1983). The model parameters that were varied are: the mean annual precipitation,QP; the sulphate deposition rate for

1982 ,SO_4; the cation exchange capacity, CEC; the weathering rates of the base cations, WECA, WENA, WEMG, WEK; the log selectivity coefficients SALCA, SALMG, SALNA, SALK; and the thermodynamic equilibrium constant for the aluminium hydroxide dissolution,KAL.

The results of the present analysis were investigated using the generalised sensitivity approach of Spear and Hornberger (1980a and b). This method compares the simulations that accurately reproduced observed features of chemistry (the "behaviour criterion") with those that did not. It then investigates the merits of the hypothesis that the set of parameters giving rise to a successful simulation and the set of parameters failing to do so have the same parent distribution. This hypothesis is tested for each parameter individually assuming them to be independent. The force with which the hypothesis is rejected is strongest for those parameters to which the achievement of a successsful result is most sensitive. A pattern recognition technique based on the Fukunaga-Koontz transformation (Fukunaga and Koontz,1970) is employed to determine any linear combinations of parameters that the model response is sensitive to. This technique has been previously applied to MAGIC by Hornberger et al.(1986) and Cosby et al.(1987).

MONTE CARLO RESULTS

Cosby et al(1986a) set up the MAGIC model to simulate one of the Loch Dee catchments.This catchment is located in the middle of the region described by cluster 1. For the present analysis we initially set up the model in the same way in order to simulate cluster 1. Table 2 indicates that for cluster 1 the effect of NO3 is small. This is possibly due to a near equilibrium between the input sources to the catchments and the plant uptake sinks within the catchment. The uptake rate was set more or less to balance the source for this simulation. The ranges from which the parameters that were drawn in the Monte Carlo analysis are shown in table 3. The mode indicates the peak for the triangular distributions (a negative mode indicates that the distribution was rectangular). The specified ranges are wide in order to encompass the entire spread of parameter combinations that are able to reproduce cluster 1 chemistry. The extent of the range is limited, however, to those values that may be experienced in the field. The behaviour constraint was chosen such that a run was considered successful if its simulated chemistry for 1982 fell within the range of values between the appropriate 5 and 95 percentiles of the cluster 1 chemistry.

Of 880 runs, 530 were successful in reproducing the features of cluster 1 regional chemistry , and these are summarised in table 3. Table 4 shows the behaviour constraint "windows" and a summary of the simulated chemistry. Figures 5 to 7 show the observed and simulated probability density functions of the cluster for Cl,SO_4 and Ca . Good fits about the mean value are seen for Ca ,Cl and SO_4 and the shapes of the simulated distributions for these three variables are also good. The fits are worst at the tail ends, resulting from either specifying a too narrow range of parameter for the Monte Carlo analysis or from the sampling of the triangular distributions failing to pick up the extremes. The simulated distribution for pH is compared to the observed distribution in figure 8.The simulation enabled the complete range of pH value, present in the region defined by cluster 1, to be reproduced. The simulated distribution is higher than the observed at the low pH end and lower at the high pH end. This bias towards reproducing the lower pH chemistry possibly lies with the model being set up to reproduce a poorly buffered, highly acidic catchment response. Whilst this is adequate for the majority of cluster 1 sites ,it may be less good for the remainder. Alternatively , a better match may also have been achieved by selecting the parameters from more sophisticated distributions than the rather crude triangular ones that were used .By matching more closely of the uppermost part of the pH distribution ,the upper tail end of the other distributions would also have been better matched.

TABLE 3 PARAMETER VARIATION FOR THE MONTE CARTLO SIMULATION

	Range for Monte Carlo variation			successful simulations			
PARAMETER	MIN	MAX	MODE	MEAN	STD	MIN	MAX
QP	1.2	3.0	2.0	1.70	.50	1.2	3.0
SO4	50	220	150	121.5	32.4	52.2	184.1
CEC	40	250	120	178.5	119.9	40.0	229.
WECA	10	250	85	69.4	45.1	10.1	162.2
WEMG	0	50	25	13.4	8.9	6.5	39.4
WENA	0	50	25	10.3	6.93	.1	29.0
WEK	0	30	10	3.7	2.53	.1	10.5
SALCA	-1	5	3	2.08	1.28	-.7	4.8
SALMG	-1	5	3	1.87	1.24	-.9	4.7
SALNA	-3	3	0	.08	1.22	-2.9	2.9
SALK	-3	3	0	.03	1.28	-2.8	2.9
KAL	8	11	9.5	9.65	.6	8.1	10.9

(WECA,WEMG,WENA,WEK and SO4 have units of meq $m^{-2}year^{-1}$,QP is in metres depth over the catchment,CEC in meq/kg)

TABLE 4 SUMMARY OF BEHAVIOUR CRITERION WINDOWS AND THE SIMULATED CHEMISTRY THAT SATISFIED THE BEHAVIOUR CRITERION FOR CLUSTER 1

	behaviour criterion windows		successful runs		
Variable	min	max	mean	min	max
pH	4.4	7.6	5.4	4.3	6.5
Ca meq/m^3	20	245	91.5	21.5	224
Mg " "	18	190	27	19	85
Na " "	10	330	196	11	372
K " "	3	35	12	3	34
SO4 " "	40	245	115	39	242
NO3 " "	9	25	16	9	22
Cl " "	79	360	203	125	401

The changes over time in the distributions of values of the simulated chemicals were ascertained by saving the output for 1844 and 1982. The future deposition was modelled as a linear decrease to 30% of the 1982 level by the year 2001. This is merely one of many possible scenarios and is used only to illustrate the potential use of the model for regional prediction . The regional levels of chemical concentrations in 2060, under this deposition sequence,were also looked at. The results are shown in figures 9-14.

For cluster 1, the MAGIC model shows a large drop in both pH an alkalinity over the past 140 years. The pH level falls by .8 pH unit and alkalinity falls by approximately 70 meq/m^3. This is in accord with the findings of Battarbee and Flower(1985), who report changes in pH level of up to 1.0 pH unit during the same period, for those lochs in the Granitic region of Galloway . A small recovery is seen during the future scenario. The small size of this recovery reflects the depletion in the soil of base cations (to between 2 and 5 % in 1982). The low rate of soil weathering in the region enable only a slow recovery rate. The sulphate distributions clearly show the shift in regional concentrations simulated as the result of industrialisation .The preindustrialised levels are between 0 and 38 meq/m^3, whereas the 1982 levels are much higher with a wider spread of values. The 2062 levels are reduced by about 30%, closely matching the decline in sulphate deposition. This confirms the status of the soil as having low sulphate adsorption capability. Aluminium is seen to increase in extent over the years,up to 36 meq/m^3 for the most acidic lakes. The majority of sites, however, show only a small increase. Of the base cations, Calcium levels are seen to rise only slightly, whereas magnesium levels show a much more substantial rise. The future scenario shows small decreases in these cations, as a result of the partial recovery of the soil.

SENSITIVITY ANALYSIS

The results of the generalised sensitivity analysis are presented in table 5 . This describes the difference between the distributions of parameters that give rise to a "behaviour" and those that do not. The Mann-Whitney statistic (M-W) indicates whether the distributions are significantly separated along the parameter axis, and the Kolmogorov-Smirnov statistic (K-S) gives the greatest separation of the two corresponding cumulative distribution functions. In both cases, a large number indicates a high significance and sensitivity of simulation to that parameter. The greatest sensitivity as indicated by these two statistics is seen for QP (M-W of 3.19) and for WECA (K-S of .219) respectively. Parameter S04, the 1982 deposition level, figures highly in both cases. WECA has a high value for the K-S statistic and a low value for M-W statistic.This indicates that one of the two distributions (behaviours or non-behaviours) is centrally placed within the domain of the other. The central distribution for WECA is the one for behaviours,showing a peaked, triangular distribution with a well defined band of acceptance. Thus,whilst the WECA parameter was outside the range 10 to 162 meq m^{-2}yr^{-1}, there was no chance of a successful simulation.

A method based on the Fukanaga-Koontz pattern recognition technique was used to look at the sensitivity with respect to linear combinations of the parameters . This analysis reveals two eigenvectors of high sensitivity. The first was more sensitive than any individual parameter, with M-W of 3.63 and K-S of .214 .The weight of each component of the normalised eigenvector indicates the relative importance of that component in explaining the variance associated with it. In this way the most important components were S04, explaining 63% of the variance ,and WECA,explaining 22%/. The results indicate that the succes of the model in reproducing the regional characteristics for areas of high acid susceptibility is strongly dependent on the selection of values for the WECA,S04 and QP parameters (the weathering rate of calcium, the sulphate deposition rate in 1982 and the mean annual rainfall during the duration of the simulation).

TABLE 5 RESULTS OF THE GENERALISED SENSITIVITY ANALYSIS

	comparison of behaviours to non-behaviours	
parameter	Mann-Whitney z statistic	Kolmogorov-Smirnov d statistic
QP	3.19	.139
SO4	2.19	.204
CEC	1.59	.105
WECA	.76	.219
WEMG	.51	.045
WENA	.26	.052
WEK	.52	.065
SALCA	.26	.079
SALMG	1.21	.096
SALNA	.24	.042
SALK	1.08	.092
KAL	.01	.054

DISCUSSION

This analysis tends to confirm both the view that the Galloway region is susceptible to acidic deposition and the view that a significant change in soil conditions has occurred during the past 140 years. Falls in pH level of up to pH unit have been discovered for the Galloway by Battarbee and Flower(1985) using the method of reconstrucion from study of diatom assemblage in the sediment of lochs. The simulation results show a drop in mean level of .8 pH unit. This is increased by the inability to match the highest portion of the 1982 pH distribution at the same time as matching its low end. This inability also spills into the simulated distribution for alkalinity, by cutting off the highest levels in the simulation. A fair view of the changes caused by the acidification processs can still be gleaned however, by noting that the lakes with higher alkalinity in 1982 are also those with the higher alkalinity in 1844. Hence the simulated results are valid for those lower alkalinity lakes that it represents well. The recovery under 30% deposition reduction in deposition is seen to be slight due to the depletion of base cation resource on the available cation exchange sites on the soil. In particular, Aluminium levels are seen to recover very little in the most highly acidified lakes.

Overall the simulation was successful using rather crude, triangular distributions for the parameters in the Monte Carlo analysis. Better reproduction of the present day distributions could have been achieved using more complicated distributions to describe the parameters,noting that certain results in the behaviour criterion are more tuned in to particular parameters.For example ,Calcium levels are strongly affected by its weathering rate and selectivity coefficient. The lack of available data for verification of the model calibration, however limits the usefulness of such a study.Without verification, fine points raised by such a simulation might be mere quirks of the model.

CONCLUSIONS

The MAGIC lumped parameter model of groundwater in catchments can be coupled with Monte Carlo trechniques to provide a useful method of simulating long term regional response to acidic deposition. The sensitivity of simulation to parameters in the model is seen to be dependent on the weathering rate of calcium,the level of deposition of sulphate and the mean annual rainfall for a region with low weathering rates and low sulphate adsorption. The response of the region to a future deposition scenario is gleaned from the model and after a prolonged period of deposition the ability of the region to recover from the historical deposition sequence is seen to decreaase throughout the lifetime of the deposition sequence.

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FIGURE 1 GALLOWAY REGION

PH DISTRIBUTION

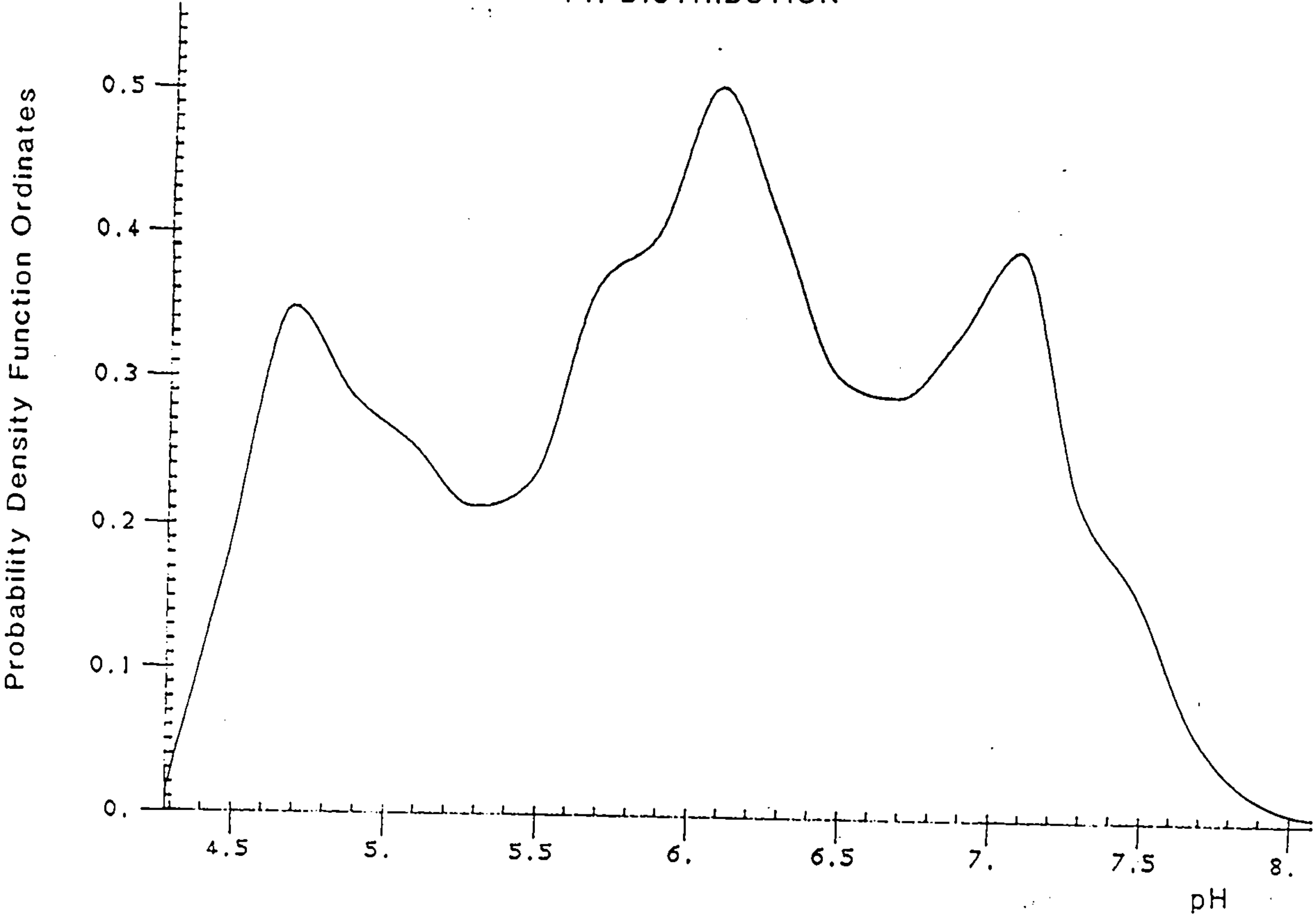


FIGURE 2 GALLOWAY REGION

CALCIUM DISTRIBUTION

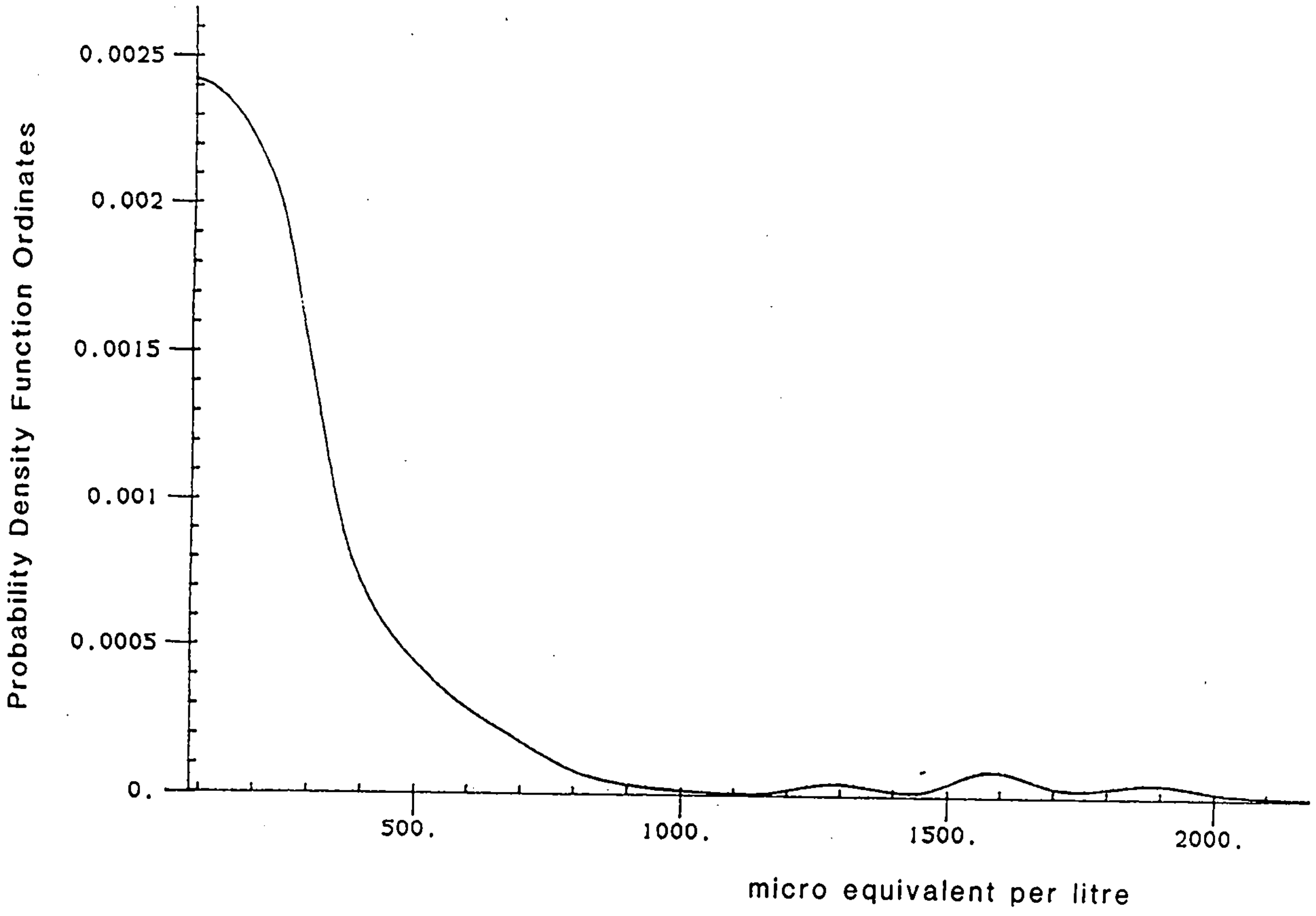


FIGURE 3 pH DISTRIBUTIONS

FOR CLUSTER 1 AND CLUSTER 2

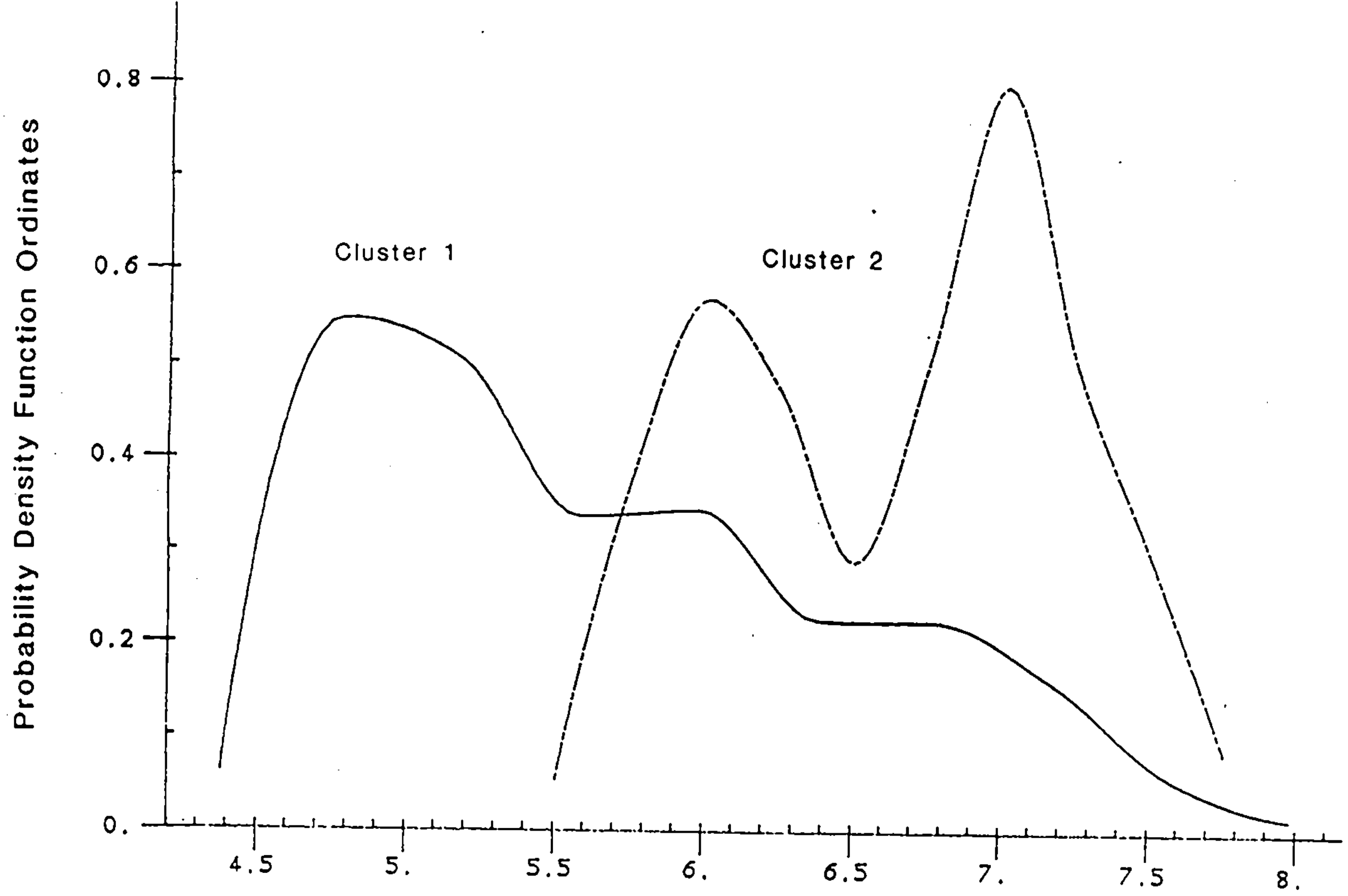


FIGURE 4 CALCIUM DISTRIBUTIONS

FOR CLUSTER I AND CLUSTER 2

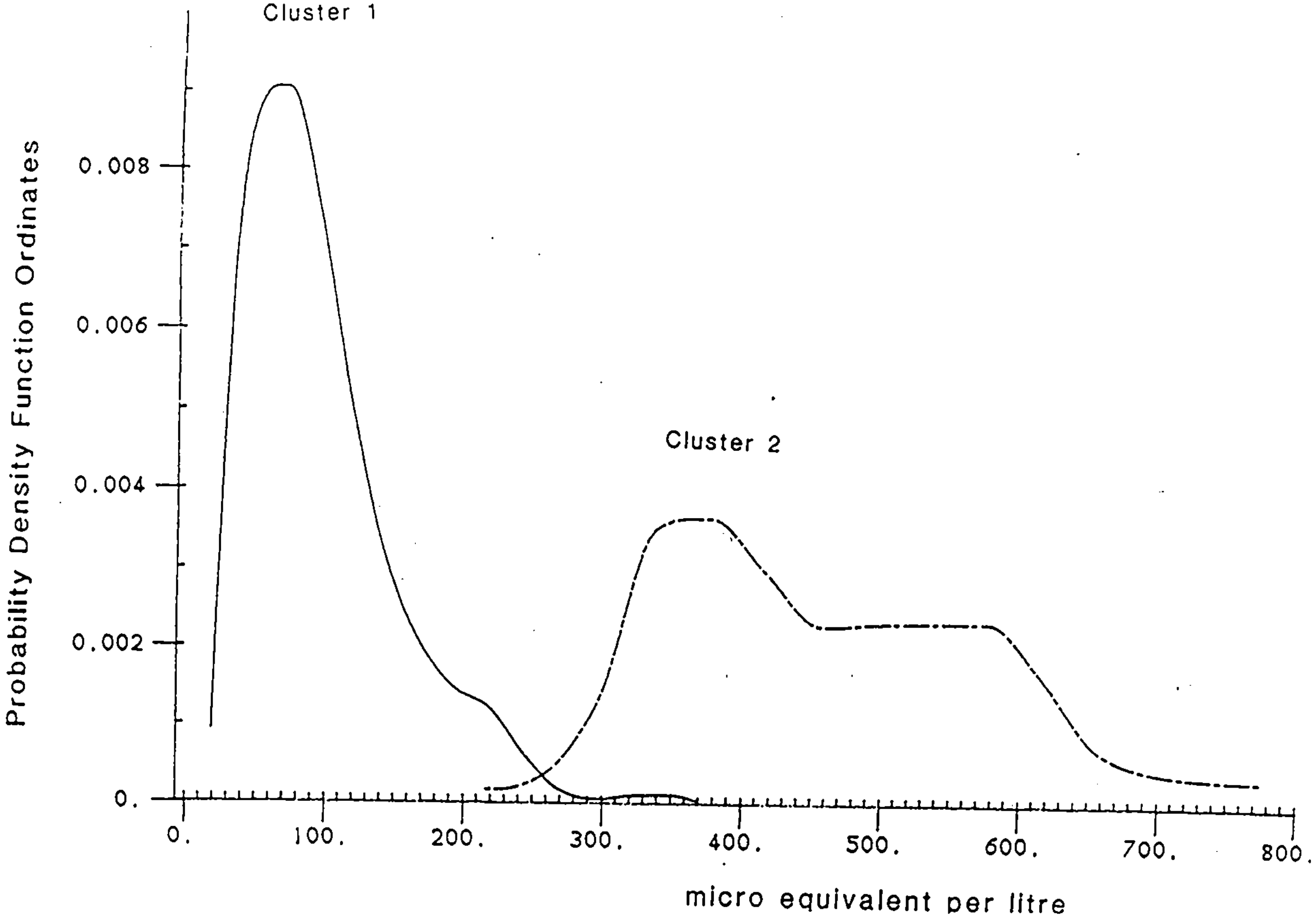
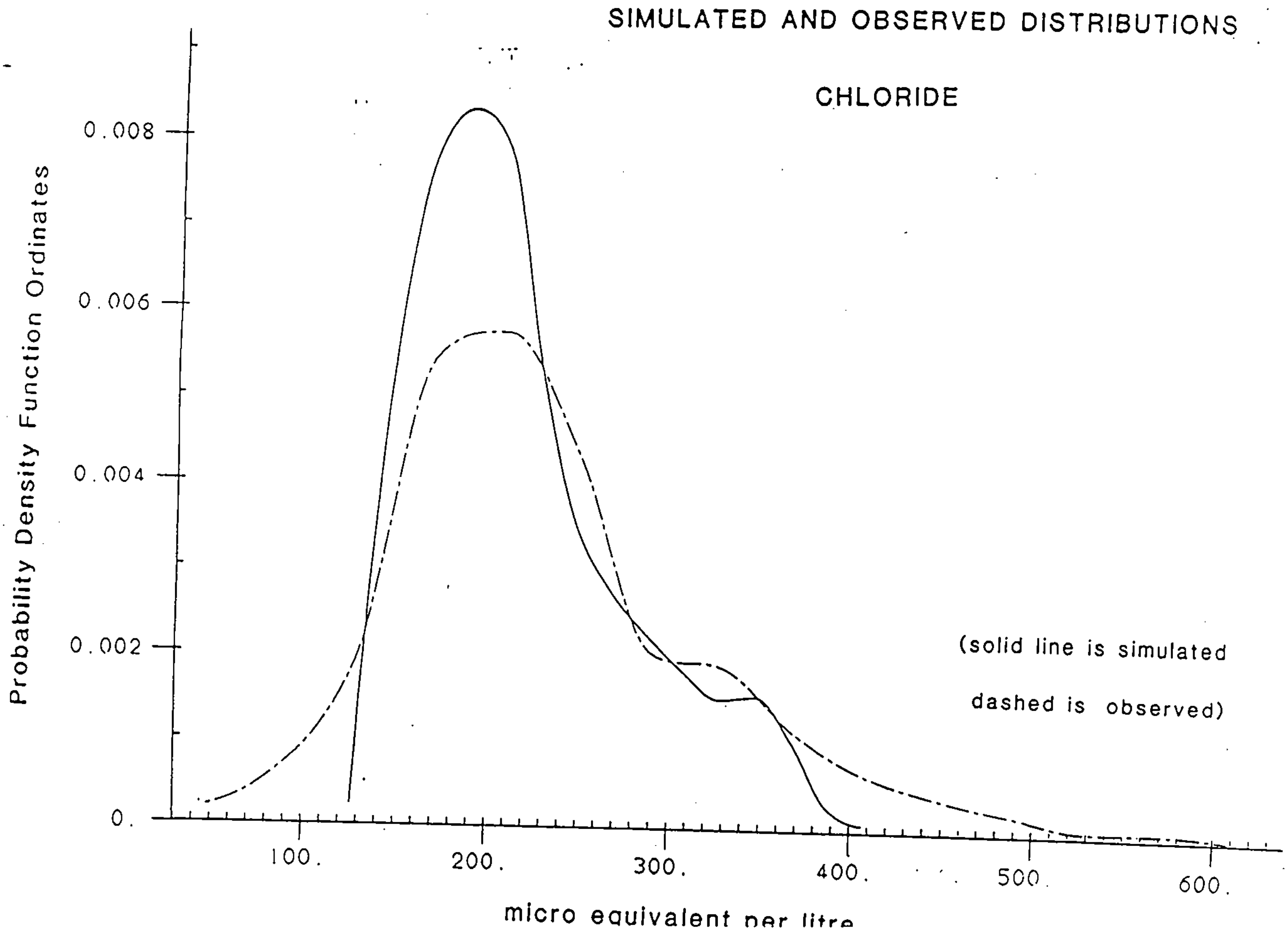


FIGURE 5 CLUSTER 1



SIMULATED AND OBSERVED DISTRIBUTIONS

CHLORIDE

(solid line is simulated
dashed is observed)

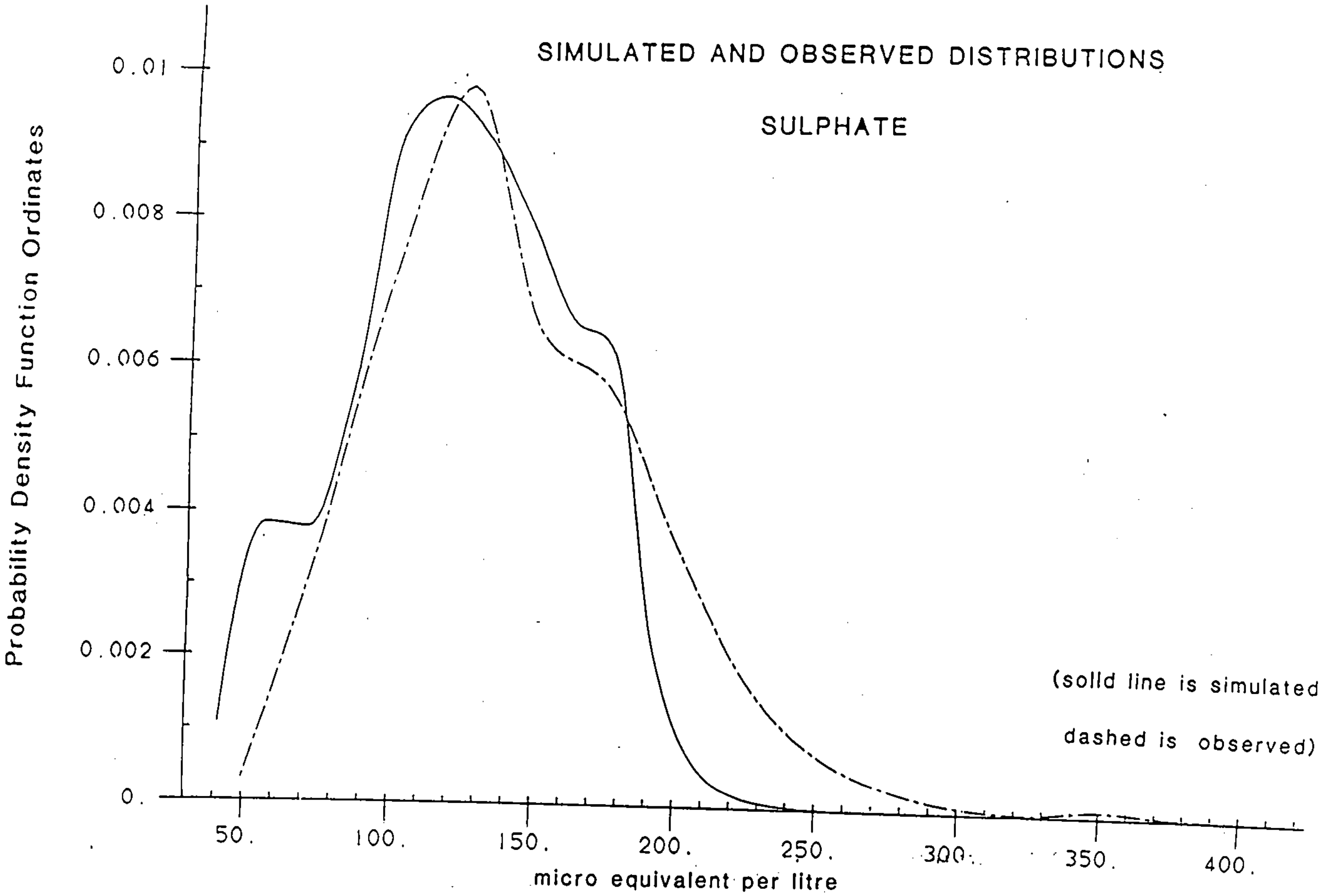


FIGURE 6 CLUSTER 1

FIGURE 7 CLUSTER 1

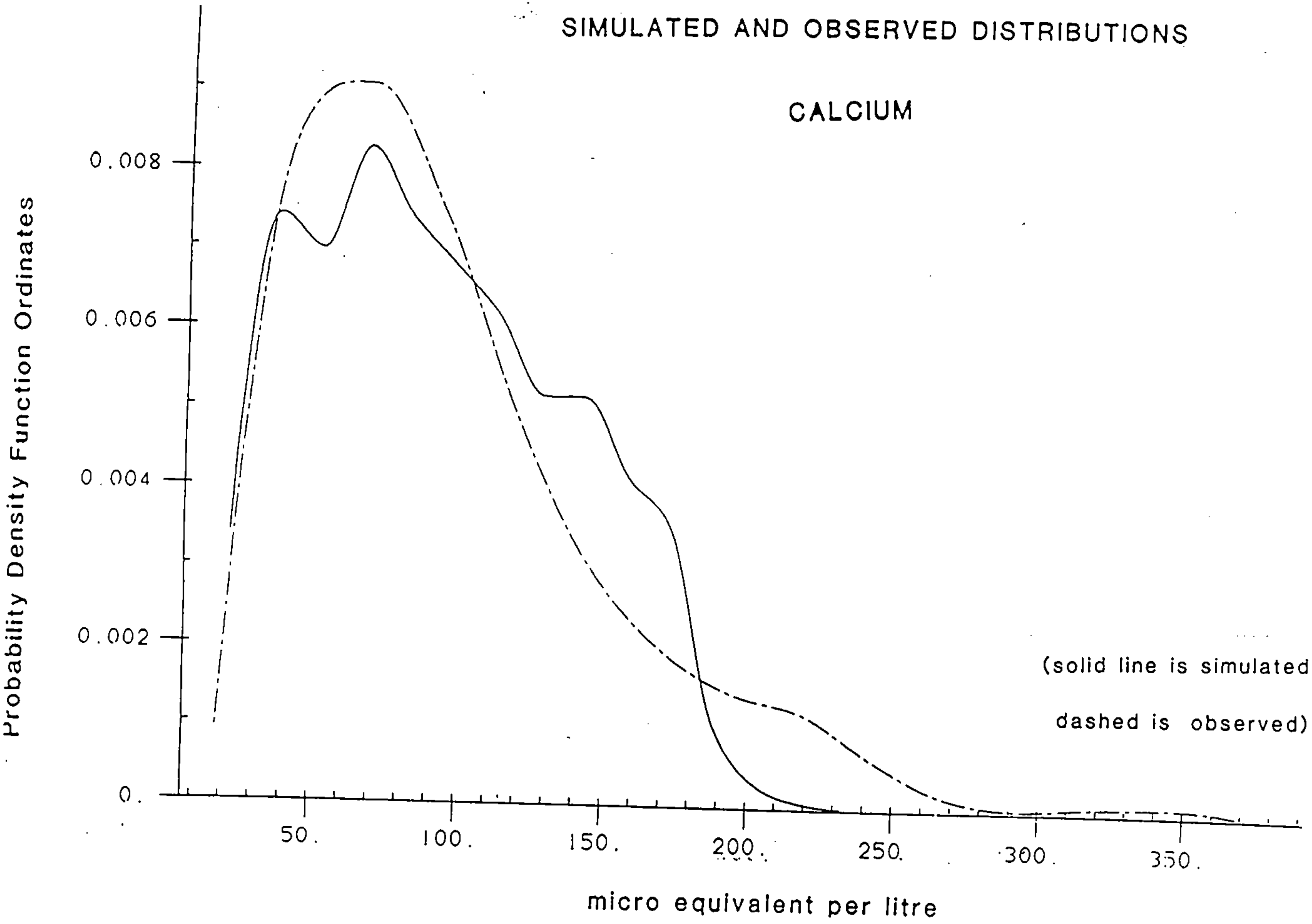


FIGURE 8 CLUSTER 1

SIMULATED AND OBSERVED DISTRIBUTIONS

pH

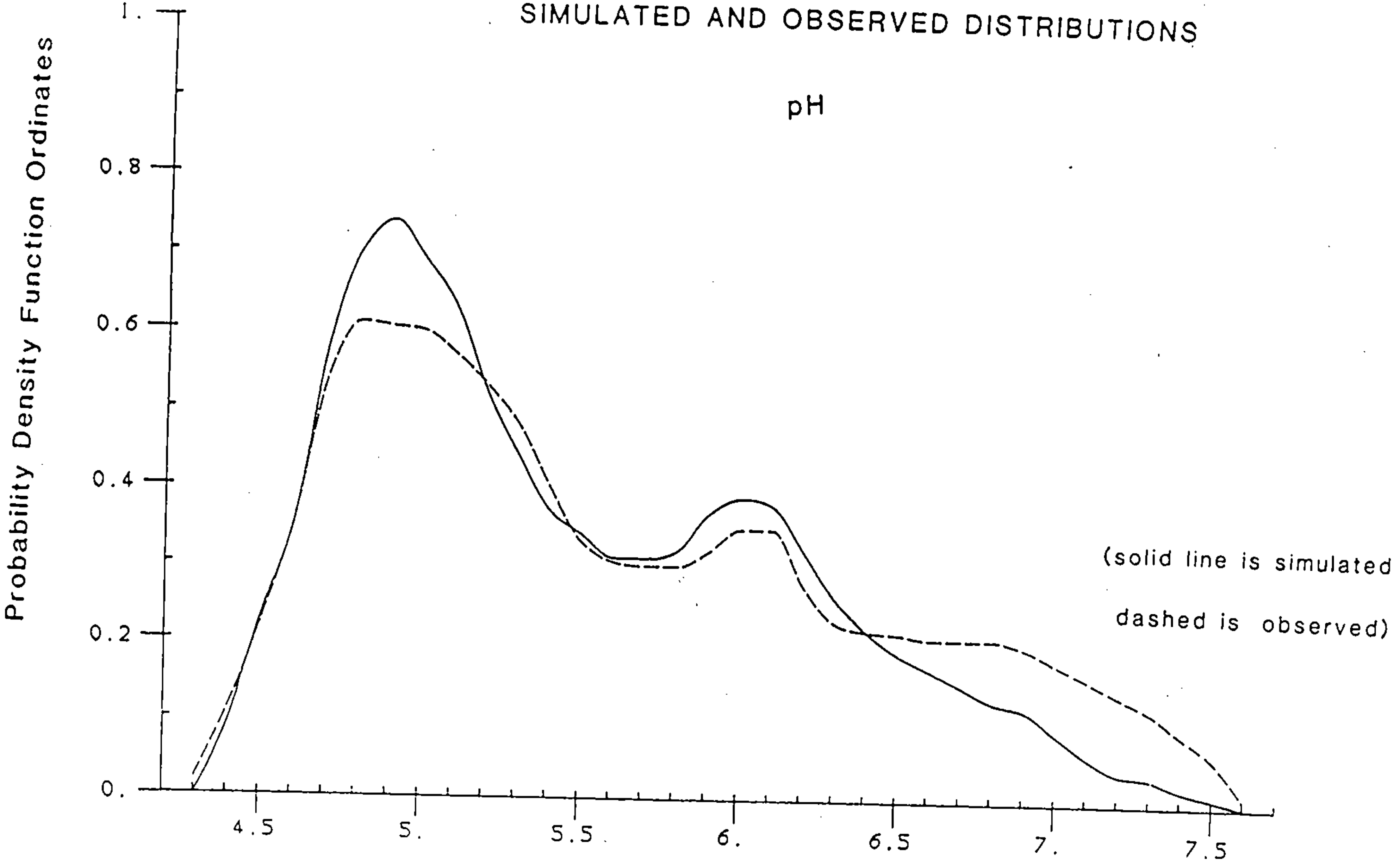


FIGURE 9 SIMULATION OF CLUSTER 1

TIME VARIATION IN DISTRIBUTION

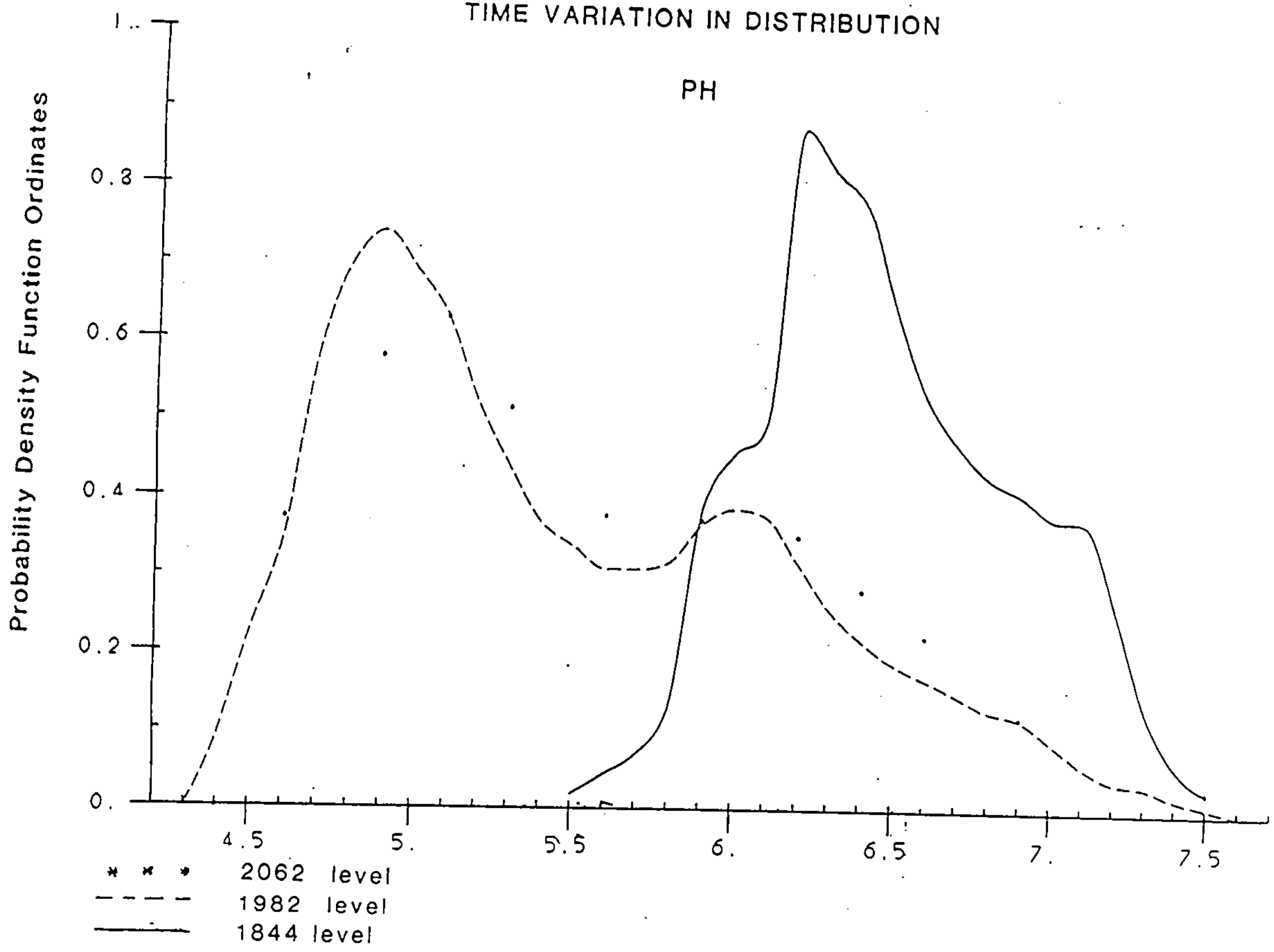


FIGURE 10 SIMULATION OF CLUSTER 1

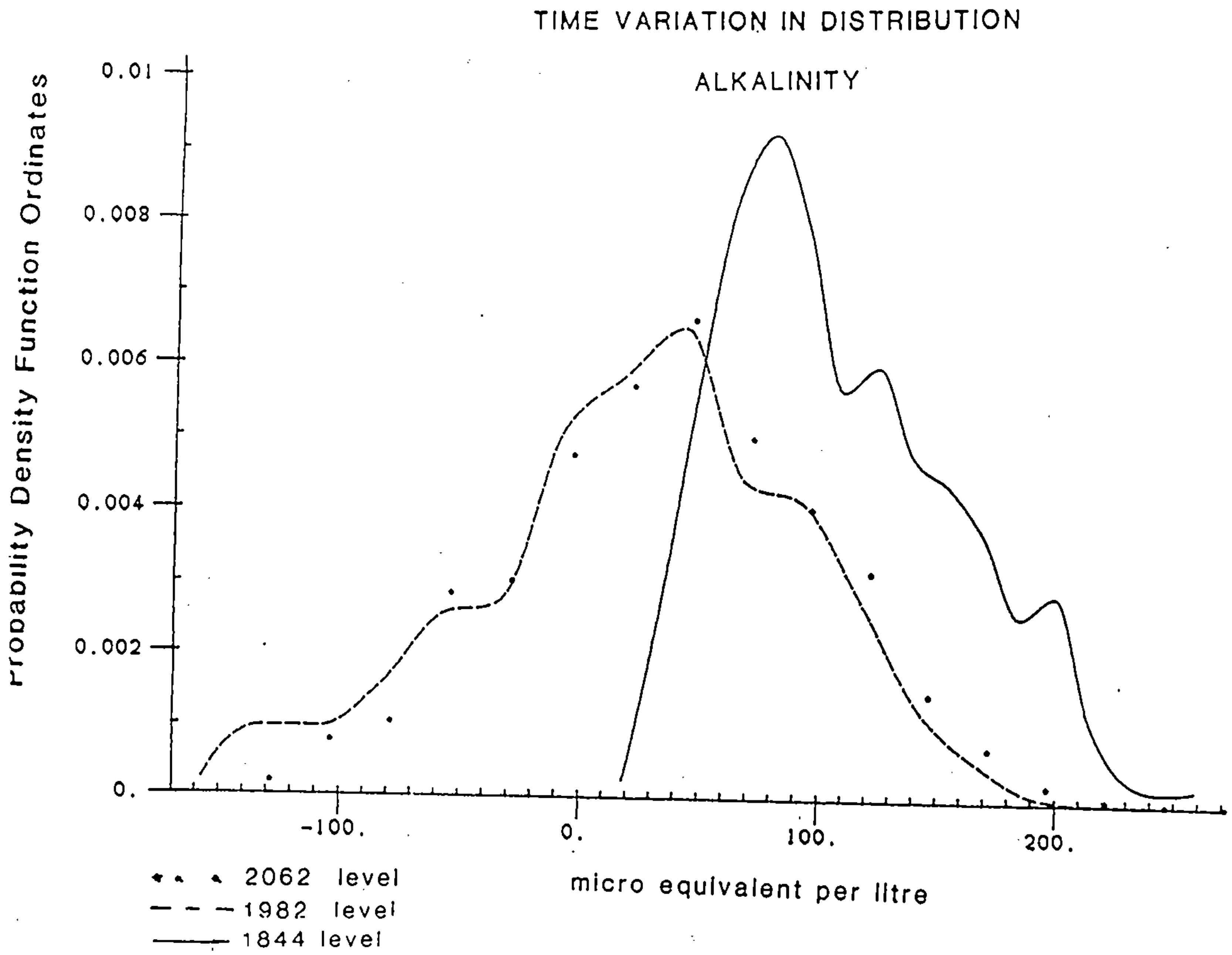


FIGURE 11 SIMULATION OF CLUSTER 1

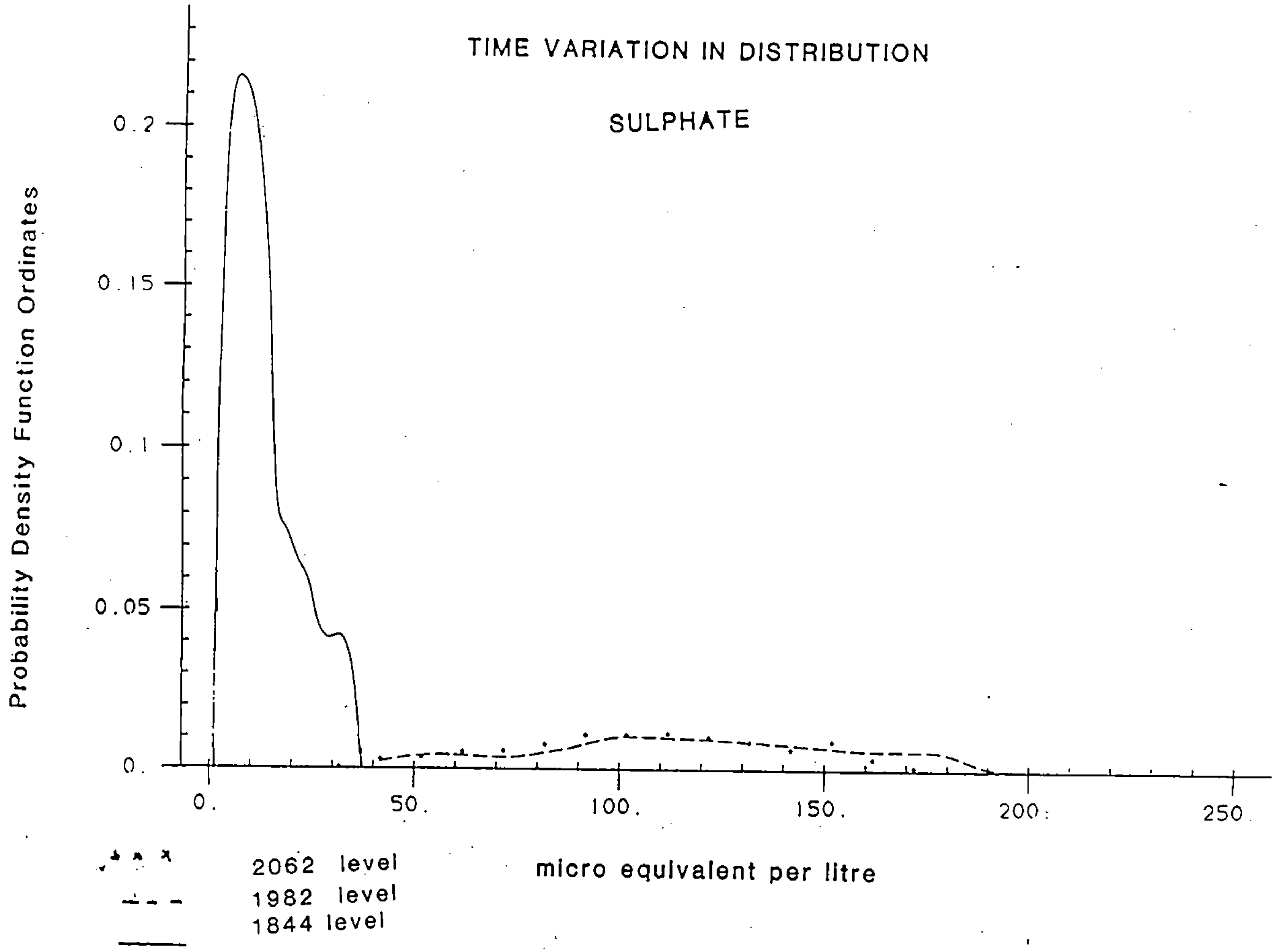


FIGURE 12

SIMULATION OF CLUSTER 1

TIME VARIATION IN DISTRIBUTION

ALUMINIUM

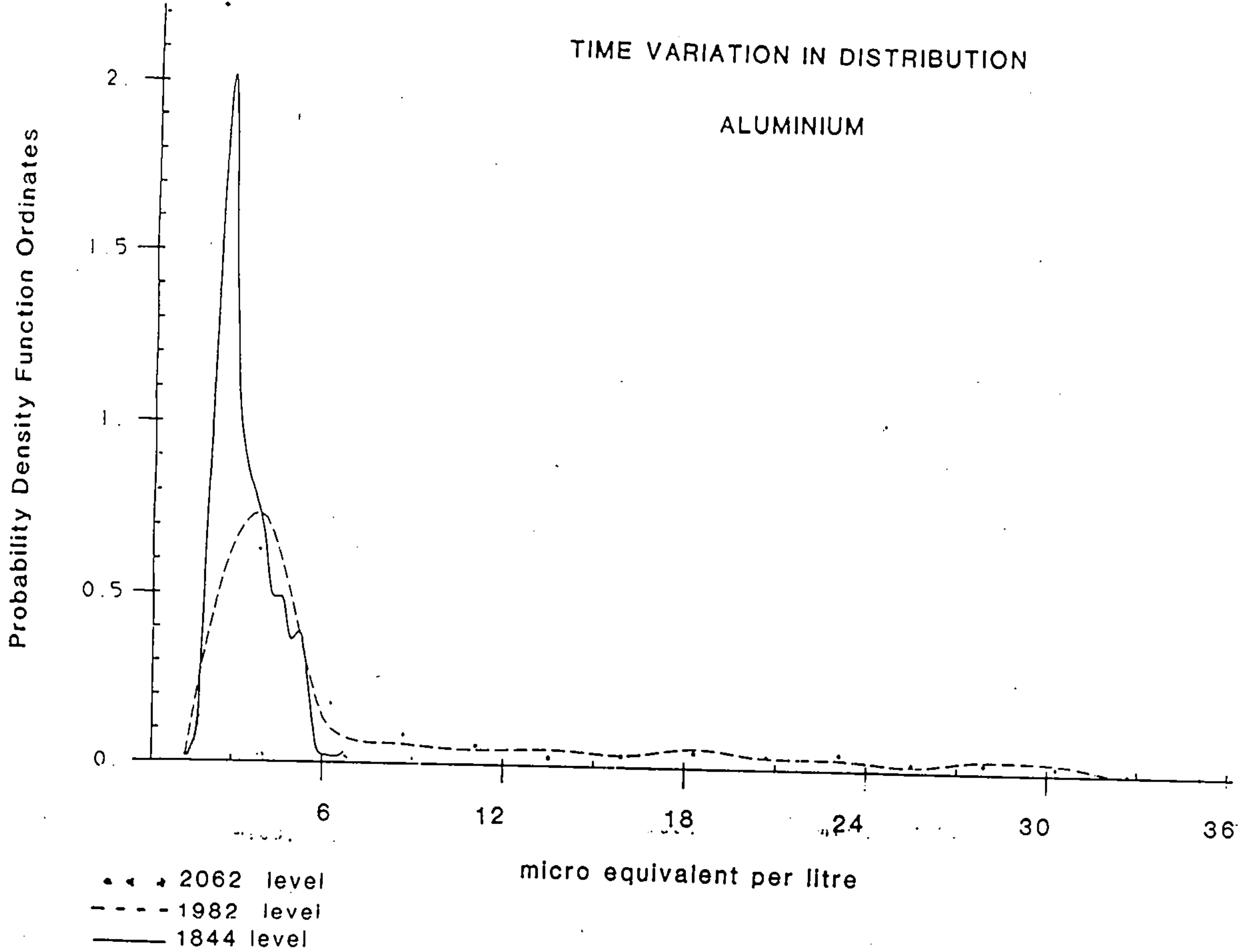


FIGURE 13 SIMULATION OF CLUSTER 1

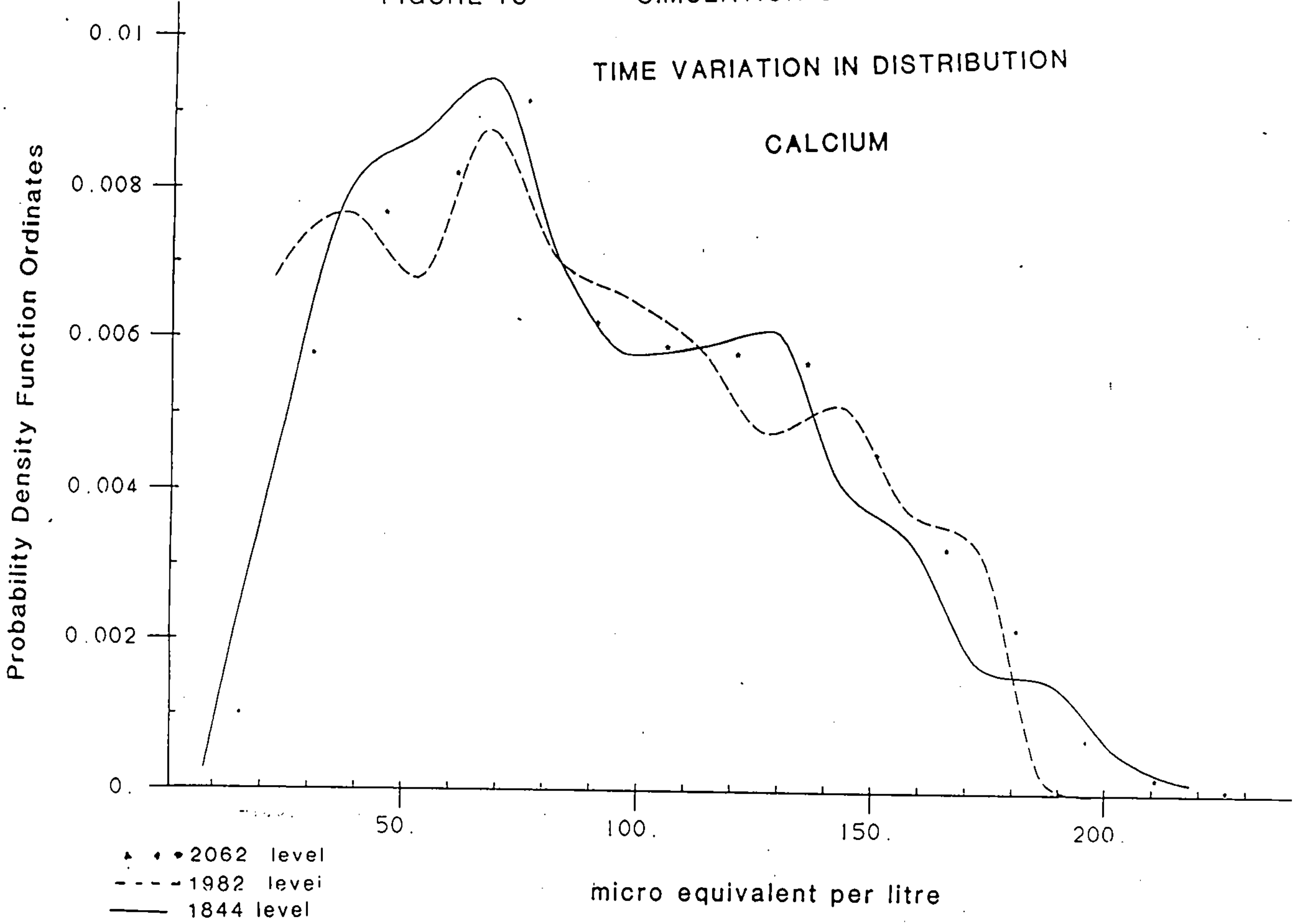
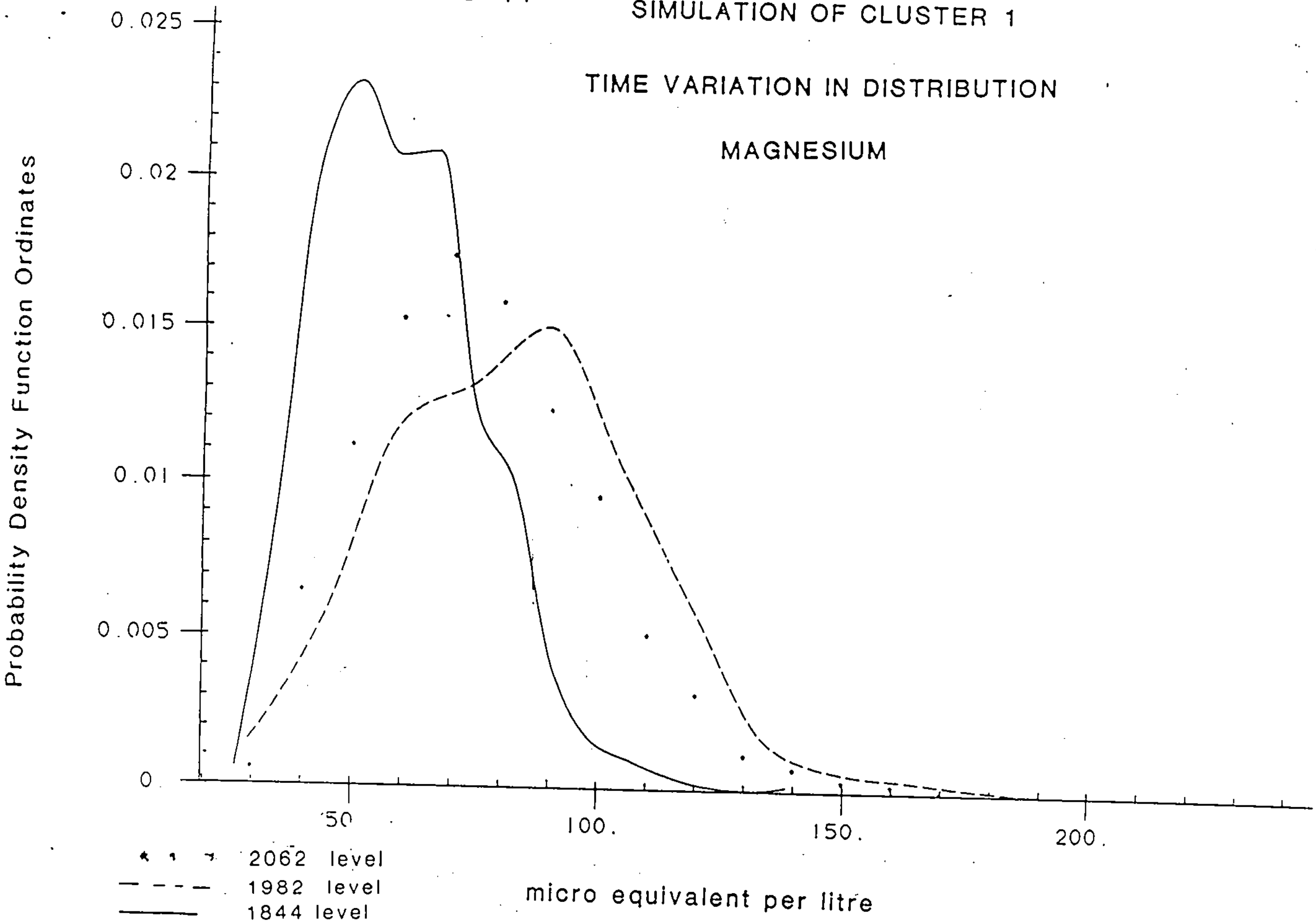


FIGURE 14


SIMULATION OF CLUSTER 1
TIME VARIATION IN DISTRIBUTION
MAGNESIUM
Probability Density Function Ordinates
0.025
0.02
0.015
0.01
0.005
0
50
100.
150.
200.
micro equivalent per litre
2062 level
1982 level
1844 level

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