Institute of Hydrology

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TOTAL IMPACT ASSESSMENT OF POLLUTANTS IN RIVER BASINS: A FEASIBILITY STUDY

by
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DOE Contract PECD 7/7/170
Total Impact of Pollutants in
River Basins

PREFACE

The report describes research completed in the first year of a contract (DOE Contract PECD 7/7/170), entitled Total Impact of Pollutants in River Basins, between the Department of the Environment and the Natural Environment Research Council (NERC). The research has been carried out at the Institute of Hydrology (IH), a component body of NERC.

Schedule 1 - Programme of Research

OBJECTIVE

To assess the sensitivity of river basin water quality to all influences, including diffuse and discrete sources of pollutants and land use change.

PROGRAMME OF WORK TO BE CARRIED OUT BY THE CONTRACTOR IN THE FIRST YEAR (1985/86)

1. The work will comprise essentially a feasibility study with a literature review of:

    a) integrated catchment hydrology and water quality models, and
    b) agrochemicals, their use, chemistry and synergistic effects.

2. The contractor will carry out some preliminary development of integrated hydrological and water quality models to represent short term and long term catchment behaviour. Preliminary validation of models will be completed using catchment data available at the Institute of Hydrology.

3. The contractor will assess the feasibility of predicting the movement and distribution of agrochemicals in a catchment, and their effects on river basin water quality.

4. A brief progress report will be required in November 1985 and a final report at the end of the contract.

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SUMMARY AND CONCLUSIONS

The overall objective of the study is to assess the sensitivity of river basins to all influences such as diffuse and discrete sources of pollutants and land use change. Needless to say this is an extremely wide brief and the first year of the research is designed to assess the feasibility of developing catchment hydrochemical models which can be used for such impact analysis.

Fortunately IH has already considerable experience developing hydrochemical models and we have undertaken research developing river basin models to investigate pollutants such as nitrates, organic matter, heavy metals, and most recently the effects of acid deposition on catchment water quality. These models will be used to investigate the sensitivity of catchments and will be used as the basis of our feasibility study on the problems of modelling agrochemicals.

A major problem in developing water quality models is to adequately describe the non-conservative nature of pollutants. There are very few, if any, pollutants that do not undergo change on entering the environment. The extent of the interactions between pollutants and physical, chemical and biological behaviour is extremely varible and it is important to bear this in mind in any impact assessment or modelling study. In this report we consider the problems of modelling nitrates, heavy metals, acidic deposition and pesticides and each of these requires different approaches to ensure that the dominant mechanisms controlling behaviour are incorporated. They also all vary in the extent to which pollutants are derived from point and diffuse sources and this is another important consideration. A brief review of the research and conclusions for each area is given here together with relelvant conclusions. Details of each component study is presented in the following report sections.

A Water Quality Model for the Thames River Basin

The Thames river basin provides the ideal test bed for a model since it contains a wide range of point sources of pollution as well as receiving pollutants from diffuse sources. An extensive water quality model for the river basin has been developed with the model accounting for tributaries, groundwater, surface runoff, effluents and abstractions. The model predicts water quality (ammonia, nitrate, dissolved oxygen, biochemical oxygen demand, any conservative pollutant) on a daily basis at 26 key sites along the Thames.

The model has been used to investigate future nitrate concentrations in the Thames and has been run using 56 years of hydrological data to reproduce river flows and nitrate concentrations at Farmoor and Datchet which are abstraction sites providing drinking water for Oxford and London respectively. The model was run assuming two sets of conditions:

(a) 1982 agricultural land use, fertiliser application rates, population levels and water demands;

(b) 2006 agricultural land use, fertiliser application rates, population levels and water demands.

The 1982 conditions were based on published land use information and fertiliser surveys and inputs from the sewage treatment plants were based on historical population and per capita consumption data. Forecasts for the 2006 conditions were made from trends in the historical data and estimates of population growth.

The results from the model runs under the two sets of conditions are summarised in Tables 1 and 2, which show the number of years the WHO limit of 11.3 mg/ℓ would be exceeded at the two abstraction sites considered. It is clear that at both abstraction sites there will be a marked increase in the number of years that 11.3 mg/ℓ would be exceeded if nothing were to be done to control the nitrate problem. It is interesting to note that although the number of years with exceedance is greater at Farmoor than Datchet in 1982, in 2006 the numbers of years of exceedance is similar, at the two sites. This may be because the nitrate load on the river downstream of Farmoor has been increased more than upstream by a larger population increase or increased fertiliser applications. Another possible explanation is that a uniform increase in nitrate load over the river has taken place but the natural denitrification processes are no longer able to remove nitrate at a sufficient rate to prevent its accumulation downstream.

The model also provides information on the relative effects of diffuse pollution. During autumn storm and winter high flow conditions the nitrate diffuse sources such as agricultural runoff completely dominated the point source pollution. The situation is altered during low flow conditions when

Simulated Nitrate Concentrations for 56-year Hydrological Sample

TABLE 1 OXFORD INTAKE ON RIVER THAMES

Duration of exceedance	No. years 11.3 mg N/ℓ exceeded (October - September) 1982 land use, population and demand	 2006 land use, population and demand
1-15 days	7	10
16-30 days	3	6
31-45 days	2	2
46-60 days	0	1
61-75 days	0	3
76-90 days	0	0
> 90 days	0	0
as annual average	0	0
Total no. years in which exceedance	12	22

TABLE 2 LONDON INTAKE ON RIVER THAMES

Duration of exceedance	No. years 11.3 mg N/ℓ exceeded (October - September) 1982 land use, population and demand	 2006 land use, population and demand
1-15 days	5	8
16-30 days	2	9
31-45 days	0	2
46-60 days	0	1
61-75 days	0	0
76-90 days	0	0
> 90 days	0	0
as annual average	0	0
Total no. years in which exceedance	7	20

the point sources are significant. However, the effects of these are considerably reduced by instream denitrification during warm summer conditions.

Other Applications of the Institute of Hydrology Quality Model (IHQM)

The multi-reach, multi-tributary dynamic flow and quality model has been set up to provide an on-line impact assessment for the Bedford Ouse system. The model is used to forecast flow and water quality along the entire 250 kms of the Bedford Ouse and has recently been extended to include the River Ivel, Ouzel, Wissey and Flit. The model has been used to investigate point source pollution from effluent discharges and used to protect water abstractions.

The Thames model is also being set up in a similar manner for Thames Water Authority to provide an on-line operational management tool.

Also, a technique for the identification of pollutant sources has been developed. This utilises information on stream velocity and dispersion characteristics and the shape of the concentration curve at a downstream site to determine the location of the pollution. The technique has been applied to experiments on the Bedford Ouse.

Heavy Metal Modelling Studies

Using an extensive data base obtained for the River Tawe in South Wales, a comprehensive catchment model has been developed for flow, suspended sediments and heavy metals (lead, zinc, nickel, iron, cadmium, manganese and copper). The model predicts daily flows and concentrations of water quality variables at a number of sites and can provide information on the percentile distribution of heavy metals in the river. The model accounts for industrial and natural sources of heavy metals and the interactions between metals in the sediments and the water column.

Acidification Studies

A particularly difficult problem in assessing the impact of pollutants on catchments is the effect of atmospheric pollution. It is only in recent years that the effect of acidic oxides on catchment water quality has become noticeable. Part of the research programme at IH has been to investigate acidification processes occurring in catchments and develop models for predictive purposes. These models have been applied to sensitive upland catchments in Scotland and are now available to assess the sensitivity of catchments to acidic deposition and land use change.

Pesticides

Pesticide and other agrochemicals present another extremely difficult area for modelling and total impact studies. Agrochemicals are being widely used to control pests and weeds and improve crop yields. Relatively little is known about their movement in river systems and many factors influence the behaviour and fate of agrochemicals after contact with the soil, including adsorption, leaching, volatilization, erosion, microbial degradation, chemical degradation and hydrolysis. All of the above are in part dependent on soil characteristics as well as the chemical characteristics of the pesticide. Moreover soil erosion in agricultural areas is a major process contributing pesticides to the aquatic environment. Other sources, however, include industrial and sewage effluent and accidental spillages. All of these factors and sources need to be taken into consideration in any general study of pesticides in catchments, and in any modelling exercise.

More specifically with regard to pesticides in rivers, the present E.E.C. drinking water standards appear vague and open to disregard since a global standard of 0.5 ug/l for the total pesticides present takes no account of the toxic nature of individual compounds.

Recent studies both in Australia and North America, meanwhile, seem to indicate that the actual losses of pesticide rarely exceed 5% of the total, applied, and as such are not alarming. However, what is of concern is the nature of the individual pesticide concentrations reaching rivers and their possible toxic effects on aquatic fauna. Clearly, storms following recent applications of pesticides represent the main period of concern since the changeover to less persistent pesticides.

The present water authority perspective on the possible pollution problems represented by pesticides varies. Thames W.A. experience "apparent" problems with the herbicides atrazine and simazine in relation to the levels present in supply waters. Yorkshire W.A., however, experience more urgent problems based on the industrial discharges of lindane in particular, from textiles manufacturers, while Anglian W.A. have some evidence of elevated atrazine levels, probably due to indiscriminate urban usage.

Finally, with regard to the possibility of modelling pesticide movement within catchments, work, in the U.S. and at IH suggests its feasibility. All such models require hydrology and chemical components, if they are to successfully model pesticide losses. Data inputs to them also require in many instances, detailed field observations and it is intended during the next phase of the project to establish catchment studies in collaboraton with water authorities and provide an adequate data base for modelling purposes.

Conclusions

There is now considerable experience at IH in developing water quality models for river basins. Models have been developed for major lowland river basins and small sensitive upland catchments. The models have been applied for both point and non-point source pollution and have been used to assess the impact of these pollutants on river water quality. The feasibility of developing models for total impact assessment of pollutants has been adequately demonstrated and future work should build on the current expertise, paying particular attention to pollutants likely to be a problem in the future, such as agrochemicals.

SECTION 1 - MODELLING A LARGE RIVER BASIN - THE RIVER THAMES STUDY

. INTRODUCTION AND OVERVIEW

The Institute of Hydrology has developed an extensive suite of modelling techniques for predicting the impact of pollutants on the River Thames. These include detailed short-term forecasting models for real-time operational use and simulation models for predicting long term trends in water quality.

The main river flow and quality model is described in section 2 and section 3 describes how tributary quality can be forecast. Section 4 describes the forecasting model with which accidental pollution or changes in effluent discharge levels can be rapidly assessed. Section 5 describes the application of the model to the nitrates problem and provides predictions on long term trends in nitrate behaviour.

2. FLOW AND QUALITY MODELLING OF THE MAIN STEM RIVER

2.1 Introduction

The main stem model has been developed to integrate upstream inputs and provide information on flow and quality at key locations along the river. The principal future uses of the model are:-

(a) to provide detailed off-line simulations of the optimal resource strategies so that adverse effects and constraint violations can be thoroughly investigated;

(b) to provide real-time forecasts of flow and quality behaviour so that short term effects of management actions can be determined.

In order to satisfy these objectives, an interactive multi-reach model has been developed for the River Thames such that the effects of changing abstraction or effluent pumping rates or effluent quality can be explored rapidly. A sophisticated plotting package has also been developed so that the effects of changes on flow and quality can be presented graphically to model users.

2.2 The Flow Model

The first stage of model development has been to divide the main stem into a series of reaches as indicated in Figure 2.1 and shown in Table 2.1. The reaches are selected on the basis of the location of tributaries, effluents, abstractions and weirs, since these all affect the mass balance and hence the quality of the river water. Table 2.1 gives information on the reach characteristics. Considerable experience gained in previous modelling studies (Whitehead et.al., 1979, 1981, 1982, 1984) has shown that such a reach structure is particularly suitable for modelling major rivers such as the Thames.

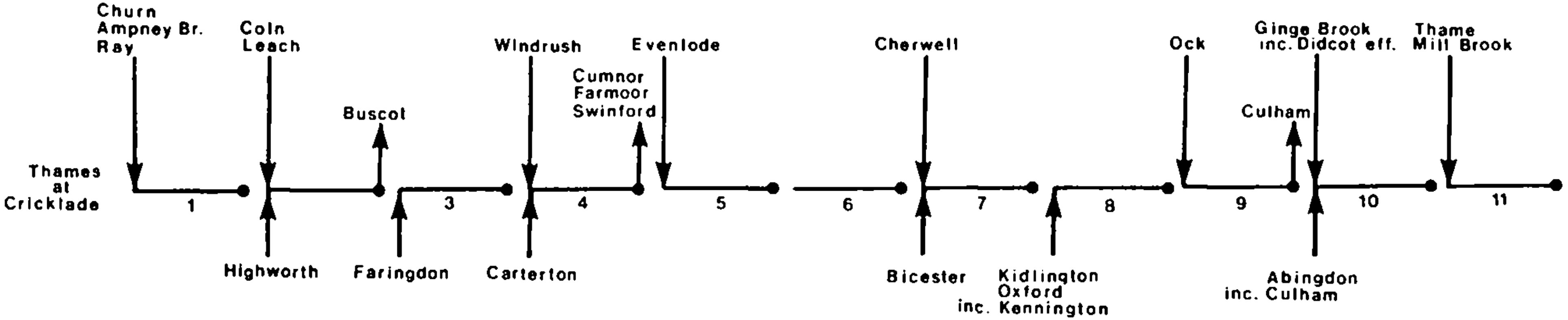


Figure 2.1 Reach structure for Thames multi-reach model

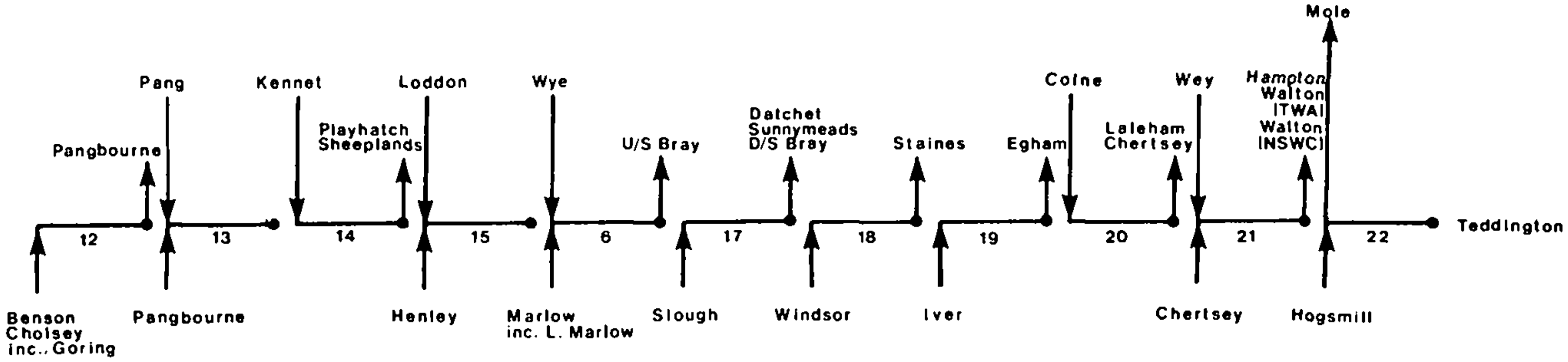


TABLE 2.1 Reach characteristics for the River Thames

Reach	Rivers Entering Reach	Effluents	Abstractions	Main River Flow Gauging Station	Water Quality Monitoring	Length km	Mean Width m	Mean Depth m	Linearised Velocity ms^{-1} $cumec^{-1}$
1 Cricklade - Castle Eaton	Thames, Churn Ampney Brook and Ray			Cricklade	H. Bridge	8.0	19.0	1.2	0.0414
2 Castle Eaton - Buscot	Coln, Leach	Highworth	Buscot			12.8	19.8	1.22	0.0413
3 Buscot - Rushey	- -	Faringdon				12.6	20.3	1.30	0.0397
4 Rushey - Pinkhill	Windrush	Carteron	Farmoor, Swinford & Cumnor	Eynsham	Swinford	20.7	25.3	1.27	0.0402
5 Pinkhill - Kings Weir	Evenlode					6.75	45.5	1.77	0.0237
6 Kings Weir - Osney						5.67	51.1	1.59	0.0199
7 Osney - Sandford	Cherwell	Bicester				13.00	85.6	2.11	0.0120
8 Sandford - Abingdon		Kidlington & Oxford				1.82	85.6	2.11	0.0120
9 Abingdon - Culham	Ock		Culham		Culham	4.14	85.7	2.01	0.0116
10 Culham - Days Weir	Ginge Brook	Abingdon, Didcot Culham		Days	Days	9.32	64.5	1.59	0.0152
11 Days Weir - Benson	Thame, Millbrook					6.38	94.0	2.29	0.0106
12 Benson - Whitchurch		Benson, Cholsey Goring	Pangbourne			18.01	109.0	2.30	0.0092
13 Whitchurch - Caversham	Pang	Pangbourne			Caversham	10.76	128.8	2.25	0.0077
14 Caversham - Shiplake	Kennet		Sheeplands & Playhatch		Sonning	8.91	124.0	2.24	0.0081
15 Shiplake - Marlow	Loddon	Henley				18.99	159.4	2.52	0.0064
16 Marlow - Bray	Wye	Marlow, Little Marlow		Bray		13.66	130.1	1.83	0.0077
17 Bray - Romney		Slough	Sunnymeads & Datchet		Datchet	8.85	105.33	1.77	0.0095
18 Romney - Bell		Windsor	Staines			9.54	88.5	1.70	0.0115
19 Bell - Egham		Iver	Egham		Egham	2.00	102.5	2.04	0.0097
20 Egham - Shepperton	Colne		Laleham & Chertsey		Laleham	8.46	104.5	1.92	0.0095
21 Shepperton - Molesey	Wey	Chertsey	Hampton and Walton (NSWC) Walton (TWA)		Walton	9.54	151.0	2.12	0.0067
22 Molesey - Teddington	Mole	Surbiton, Hogsmill		Teddington	Teddington	4	185.9	2.44	0.0054

In order to model water quality it is necessary to first simulate streamflow in all the reaches of the river shown in Figure 2.1. In the Thames streamflow model each reach is characterised by a number of cells and the model for flow variations in each cell is based on an analogy with the lumped parameter equations for the variations in concentration of a conservative pollutant under the assumption of uniform mixing over the cell (Whitehead et al, 1979). The model may be viewed in hydrological flow routing terms as one in which the relationship between inflow I, outflow, Q, and storage, S, in each cell is represented by the continuity equation:

$$\frac{dS}{dt} = I - Q \qquad (2.1)$$

with

$$S = \tau Q$$

where τ is a travel time parameter. In order to represent the variation in travel time with flow; τ is expressed as

$$\tau(Q) = \frac{L}{UN} \qquad (2.2)$$

where N is the number of compartments in the reach, L is the reach length and U, the mean flow velocity in the reach, is related to discharge through

$$U = a\,Q_m^b \qquad (2.3)$$

where Q_m is the mean flow in the reach and where a and b are coefficients to be estimated.

The value of N affects the relative importance of floodwave advection and dispersion in a reach; values of N, a and b can be determined by calibration on an observed record of downstream flow or from tracer experiments (see Whitehead et al, 1984).

Given information on upstream and tributary inputs, the flow routing model can be used to derive simulations of downstream flow by solving the differential equation (2.1). The equation is solved using a numerical integration technique which contains an automatic adjustment to the integration step length. This is particularly useful since under periods of low flow and high residence times, the integration step length can be increased thereby saving computer time. Under high flow conditions, however, residence times are reduced and in order to solve the equation to the same accuracy, it is necessary to reduce the integration step length. Since this is achieved automatically, there are relatively few numerical integration problems. Figure 2.2 shows simulated flow compared to observations for the years 1974, 75 and 76; 94% of the variance is explained and the model provides a sound basis for subsequent water quality studies.

2.3 Modelling Water Quality

The water quality models for the River Thames are based on a mass balance principle but include factors to allow for the non-conservative nature of water quality variables. For example dissolved oxygen in the river is a balance between the various sources and sinks of oxygen. On the one hand there is oxygen supplied by the reaeration from the atmosphere and photosynthetic oxygen produced by plants and algae and, on the other hand, oxygen is being consumed by respiration processes and the removal of oxygen during nitrification of ammonia or breakdown of organic material and effluents. The basic mass balance equations required to simulate water quality behaviour are as follows:

Chloride or any conservative determinand

$$\frac{dx_1(t)}{dt} = \frac{u_1(t)}{\tau(t)} - \frac{x_1(t)}{\tau(t)} + S_1(t) \qquad (2.4)$$

Nitrate

$$\frac{dx_2(t)}{dt} = \frac{u_2(t)}{\tau(t)} - \frac{x_2(t)}{\tau(t)} - k_1\, x_2(t) + S_2(t) \qquad (2.5)$$

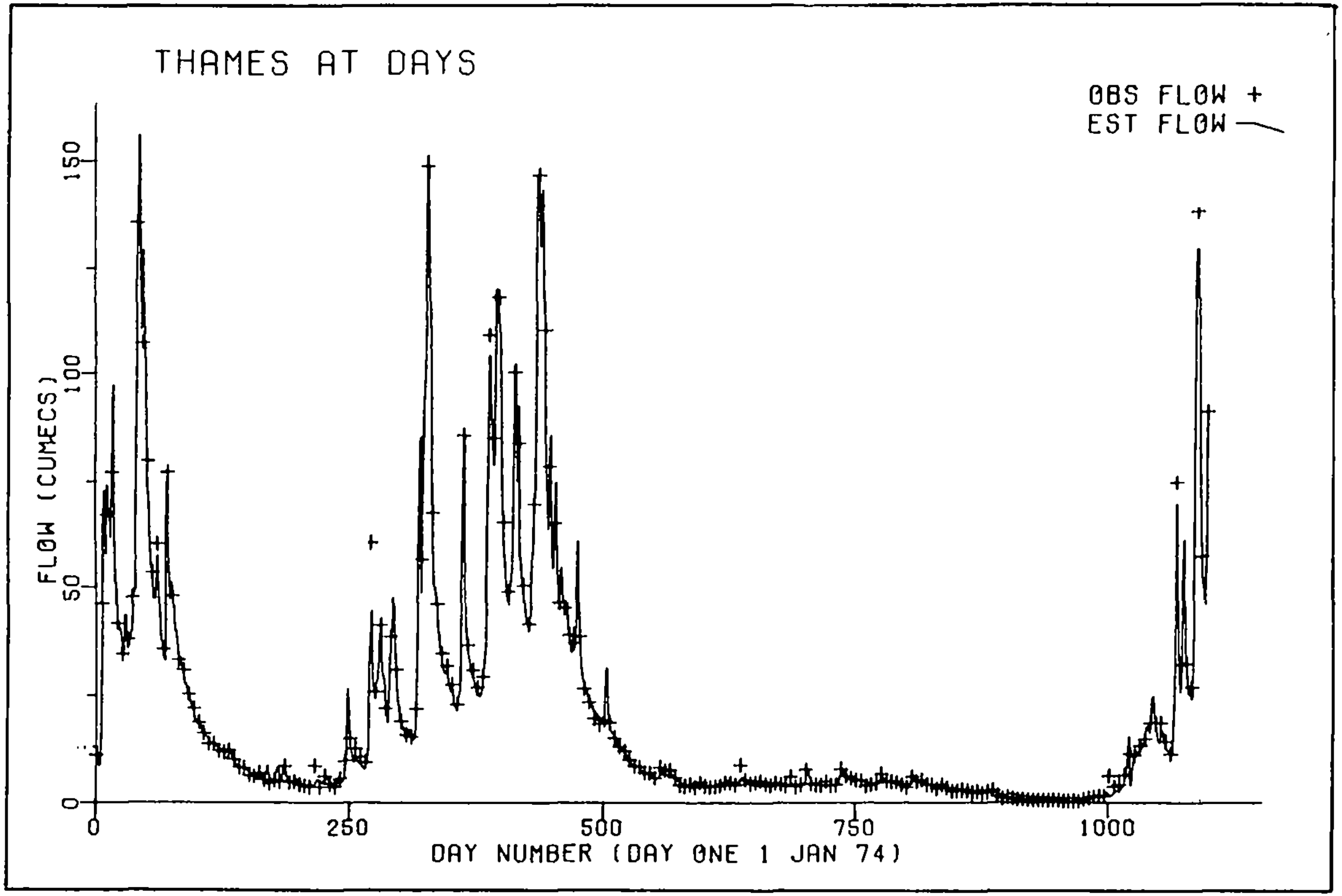


Figure 2.2 Observed and simulated daily flows at Day's Weir for 1974, 75 and 76.

Ammonia

$$\frac{dx_3(t)}{dt} = \frac{u_3}{\tau(t)} - \frac{x_3(t)}{\tau(t)} - k_2 \left(\frac{1}{Q_o(t)}\right) x_3(t) + S_3(t) \qquad (2.6)$$

Dissolved Oxygen (DO)

$$\frac{dx_4(t)}{dt} = \frac{u_4}{\tau(t)} - \frac{x_4(t)}{\tau(t)} - 4.33\, k_2 \left(\frac{1}{Q_o(t)}\right) x_3(t) - k_3\, x_5(t)$$

$$+ k_4\, (C_s(t) - x_4(t)) + S_4(t) \qquad (2.7)$$

Biochemocal Oxygen Demand (BOD)

$$\frac{dx_5(t)}{dt} = \frac{u_5}{\tau(t)} - \frac{x_5(t)}{\tau(t)} - k_3\, x_5(t) + S_5(t) \qquad (2.8)$$

where x refers to the downstream (reach output) concentration mg ℓ^{-1};
u refers to the upstream (reach input) concentration mg ℓ^{-1};
Q is the flow rate (determined from the flow model);
τ is the reach residence time (varying as a function of flow)
S refers to the additional sources and sinks affecting water quality such as the net rate of addition of DO in the reach by photosynthetic/respiration activity of plants or inputs via tributaries and effluents
Cs is the saturation concentration of dissolved oxygen, and k_1, k_2, k_3 and k_4 are the rate coefficients of the various reactions.

The rate coefficients are not constants but generally vary as a function of temperature or other variables such as depth. For example, the denitrication rate k_1 is

$$k_1 = \frac{0.05}{d}\, 10^{\,0.0293\,\theta} \qquad (2.9)$$

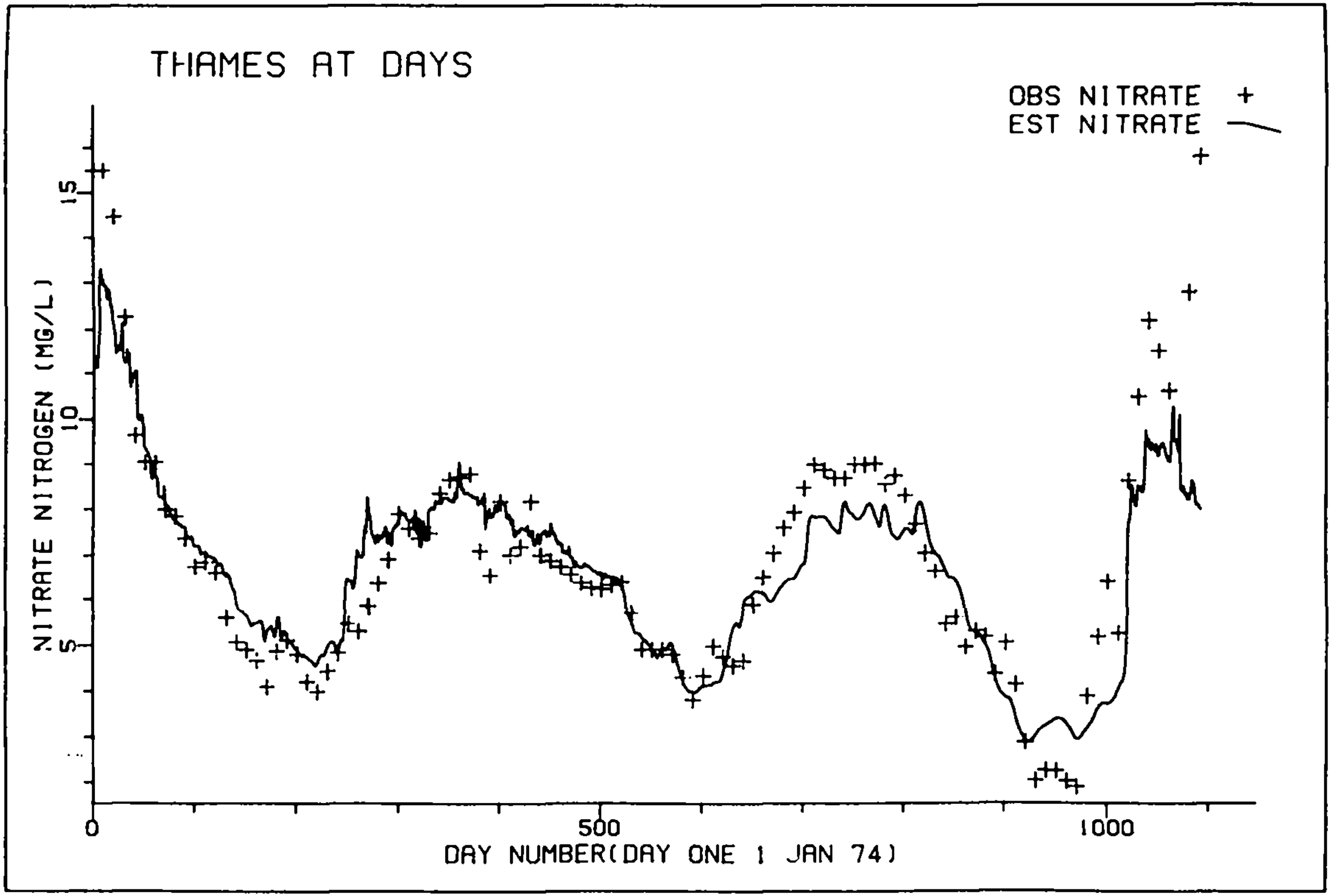


Figure 2.3 Simulated and Observed Nitrate (NO_3 as N) concentrations at Days Weir, 1974-1976 allowing for temperature dependent denitrification processes.

where d is river depth in metres and θ is water temperature in °C. A typical simulation of nitrate concentrations in the Thames is given in Figure 2.3.

The equations (2.7) and (2.8) for DO and BOD are simplifications of the real behaviour of these variables in the river. Appendix I gives a review of DO and BOD models and a description of the equations developed for the River Thames based on TWA water quality data.

2.4 Computational Aspects

The flow and quality models have been set up initially in an interactive conversational mode on a mini computer, the DEC PDP 11/23. The programs have been written in FORTRAN IV under the DEC RT-11 operating system. Some system-dependent software has been written in MACRO II assembler where FORTRAN would have been impractical. Extensive use of graphic facilities are made so that the effects of system changes on flow and water quality can be rapidly assessed. A detailed users' guide for the Thames River Management Modelling System is given in Appendix II.

QUALITY FORECASTING OF MAJOR TRIBUTARIES

An essential requirement of any forecasting system is some estimate of the input variables. In the case of the Thames model the major tributary inflows are required together with information on water quality. Assuming forecasts of flow will be available for sub-catchment models it is necessary to establish relationships between flow and water quality such that quality forecasts can be derived.

One approach to this problem is to make use of the correlation structure between flow and the water quality variables. As part of the Bedford Ouse Study (Whitehead and Young, 1979) synthetic water quality data was generated using a two stage approach as indicated in Figure 3.1. Data were analysed initially to determine the instantaneous cross-correlation pattern with the serial correlation pattern being analysed using time series techniques. Thus generating synthetic water quality data involved operating on a white noise series with appropriate transformations to reconstruct both the serial and cross-correlation structure.

In the case of the Thames we have found that there is a very strong correlation between flow and tributary water quality and therefore a simplified approach can be adopted. Figures 3.2, 3.3 and 3.4 show three typical scatter diagrams between flow and dissolved oxygen and nitrate loads respectively. In each case a high correlation is obtained and fitting a regression line to the log transformed data gave relationships of the following form

$$L = a\,Q^{b}$$

where Q is the tributary flow, $m^3 sec^{-1}$, Load is Q x C where C is concentration mg ℓ^{-1} and a and b are constants. The relationships have been used directly in the model to estimate tributary loads given estimates of flow. Typical simulations of nitrate and chloride load for two tributaries are shown in Figures 3.5 and 3.6 and in each case satisfactory estimates are obtained. Whilst far more sophisticated techniques could be employed, it is unlikely that any technique could give a better estimate of quality especially given the inevitable errors associated with sampling and measuring water quality which can be in the order of 5 to 10% (see Whitehead et al, 1981).

4. INTERACTION MODEL FOR ANALYSING ALTERNATIVES

As previously discussed the model has been set up on the mini-computer in an interactive mode. Full details of the interactive features are given in Appendix II but in this section, two examples of model applications are presented.

4.1 Effects of Changing Abstraction Rate

The model incorporates all the abstractions and effluents affecting the main stem and the effect of changes in flow and quality of any of these can be investigated. In order to illustrate this the effect of increasing the Dachet abstraction is shown in Figures 4.1 and 4.2. The abstraction has been increased by 0.6 cumecs over the period 10/6/76 to 29/6/76 and the effect this has on the downstream flow at Egham is indicated in Figure 4.1. The flow falls

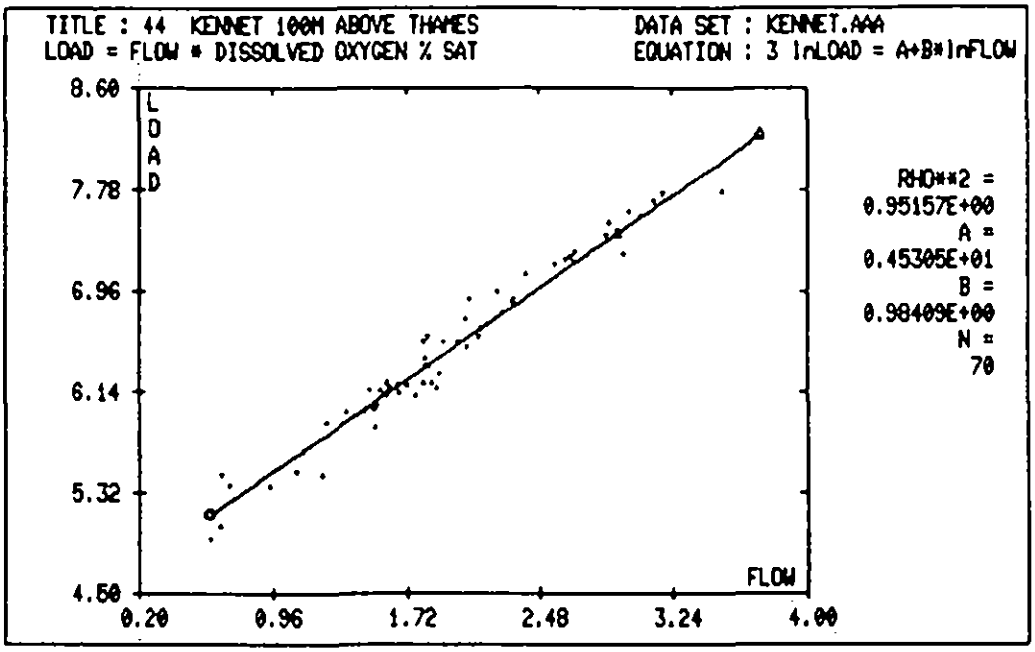


Figure 3.2

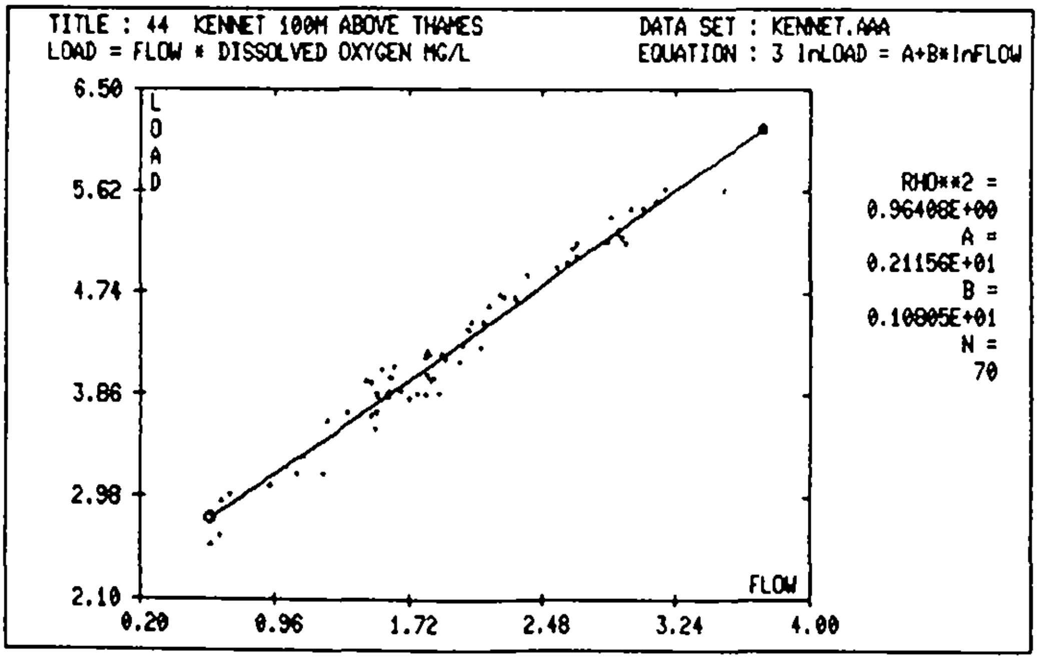


Figure 3.3

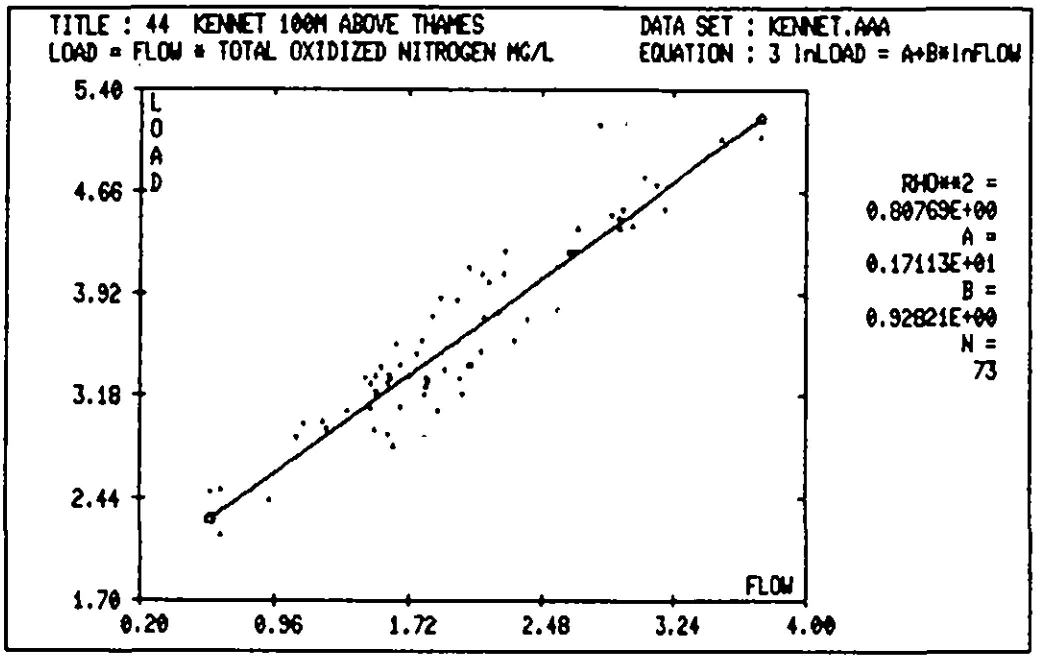

TITLE : 44 KENNET 100M ABOVE THAMES
LOAD = FLOW * TOTAL OXIDIZED NITROGEN MG/L
DATA SET : KENNET.AAA
EQUATION : 3 lnLOAD = A+B*lnFLOW
LOAD
5.40
4.66
3.92
3.18
2.44
1.70
0.20
0.96
1.72
2.48
3.24
4.00
FLOW
RHO**2 =
0.80769E+00
A =
0.17113E+01
B =
0.92821E+00
N =
73

Figure 3.4

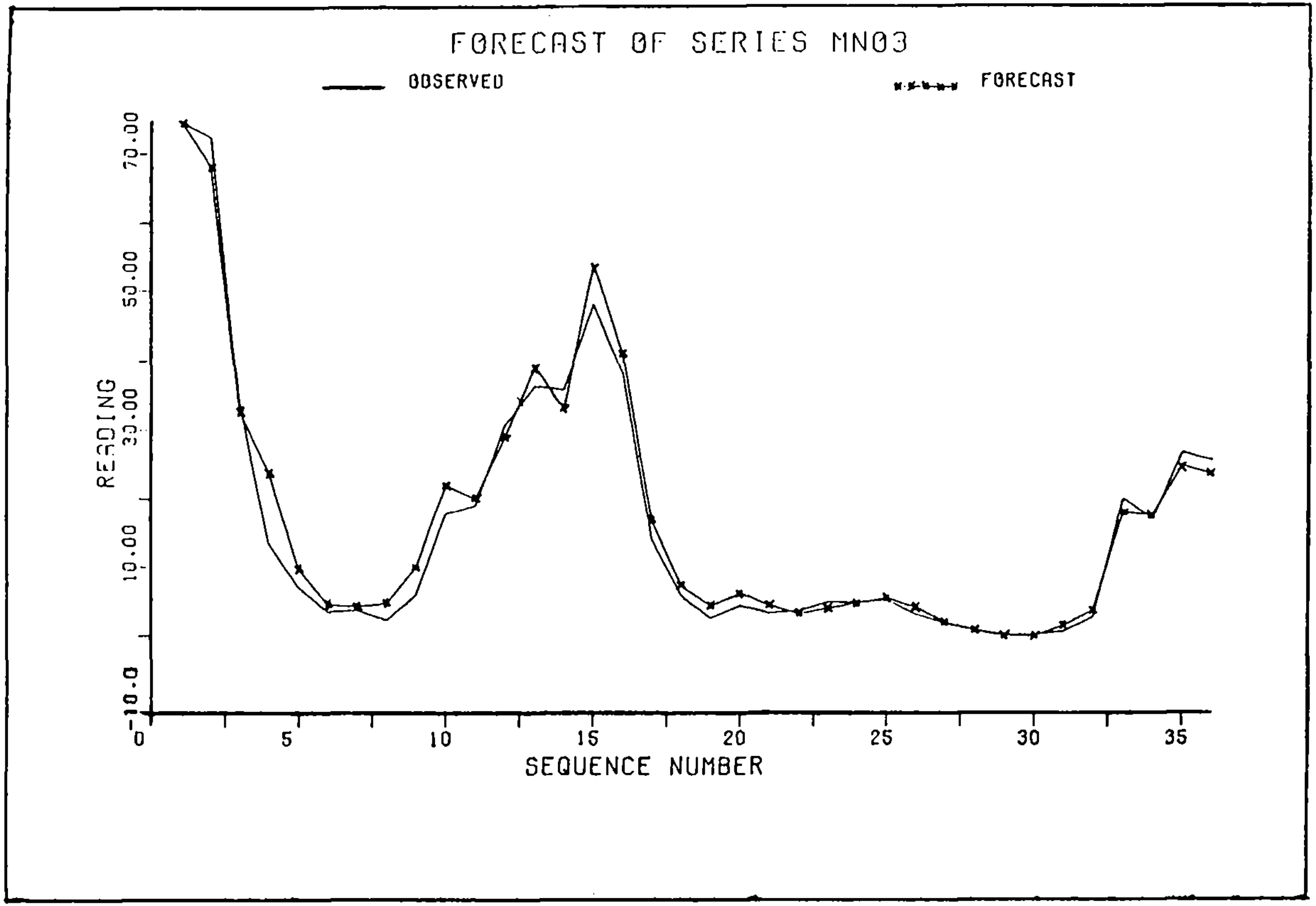


Figure 3.5 Simulated and observed nitrate mass load for the River Windrush, a tributary of the River Thames

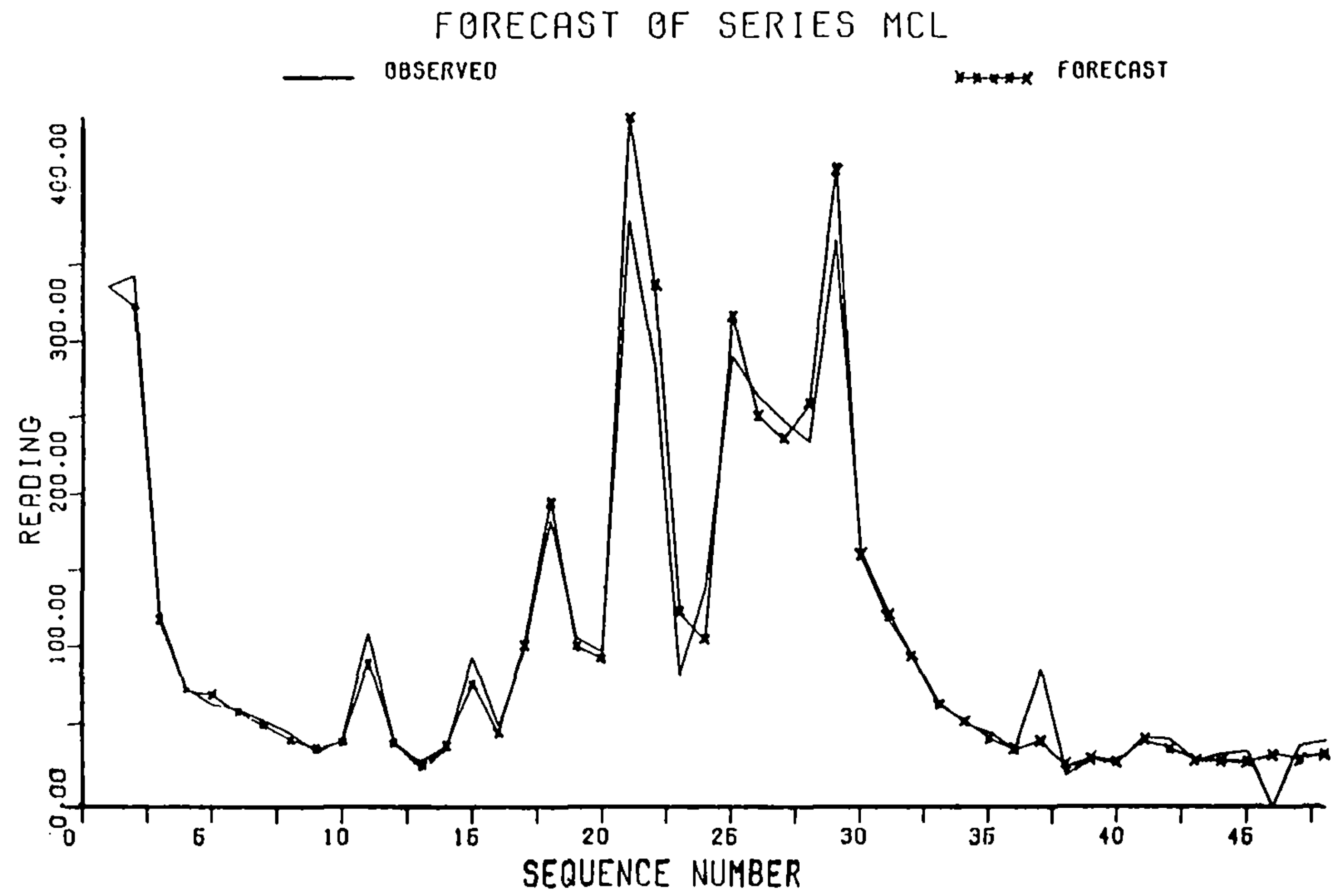
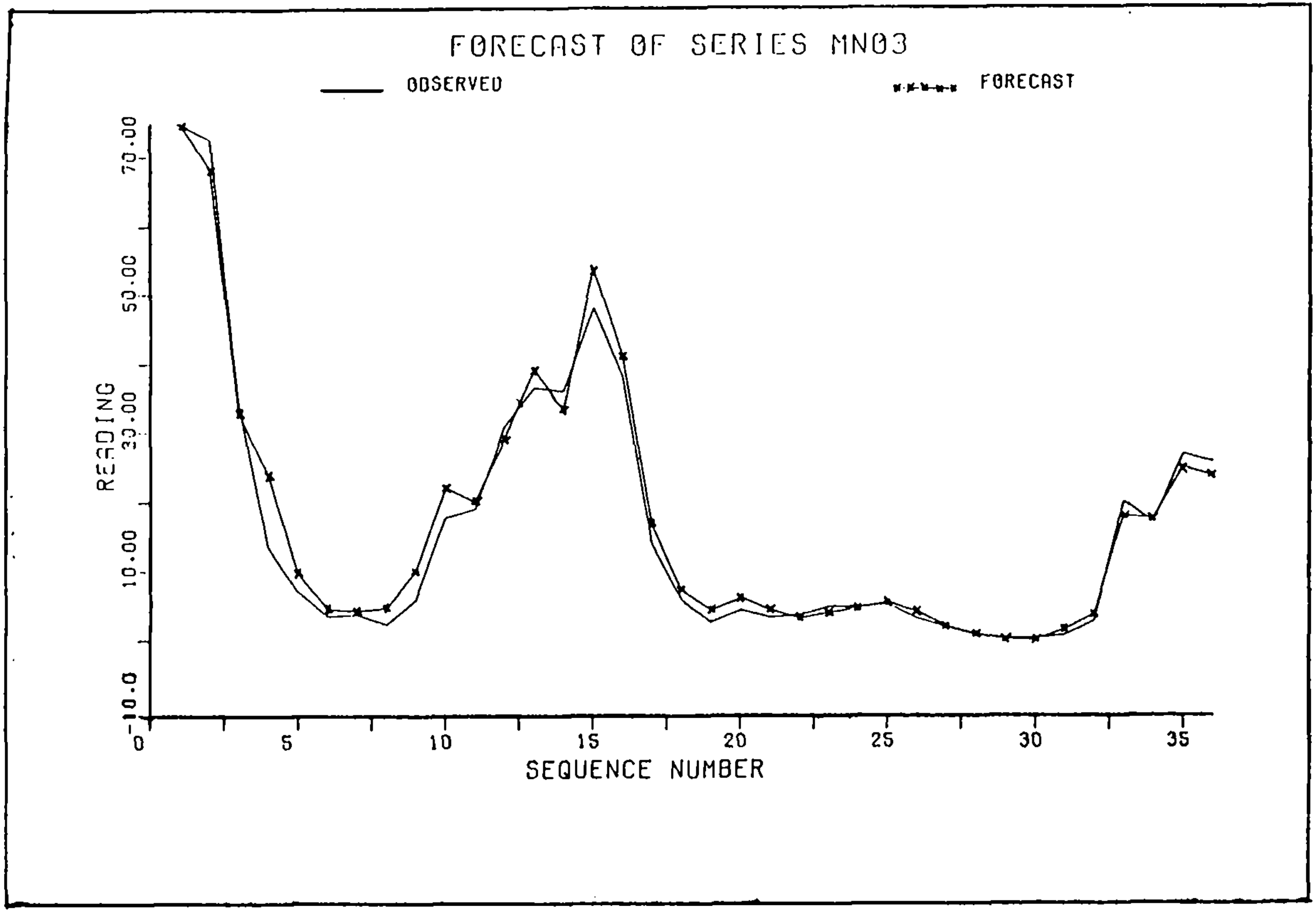


Figure 3.6 Simulated and observed chloride mass load for the River Cherwell, a tributary of the River Thames.



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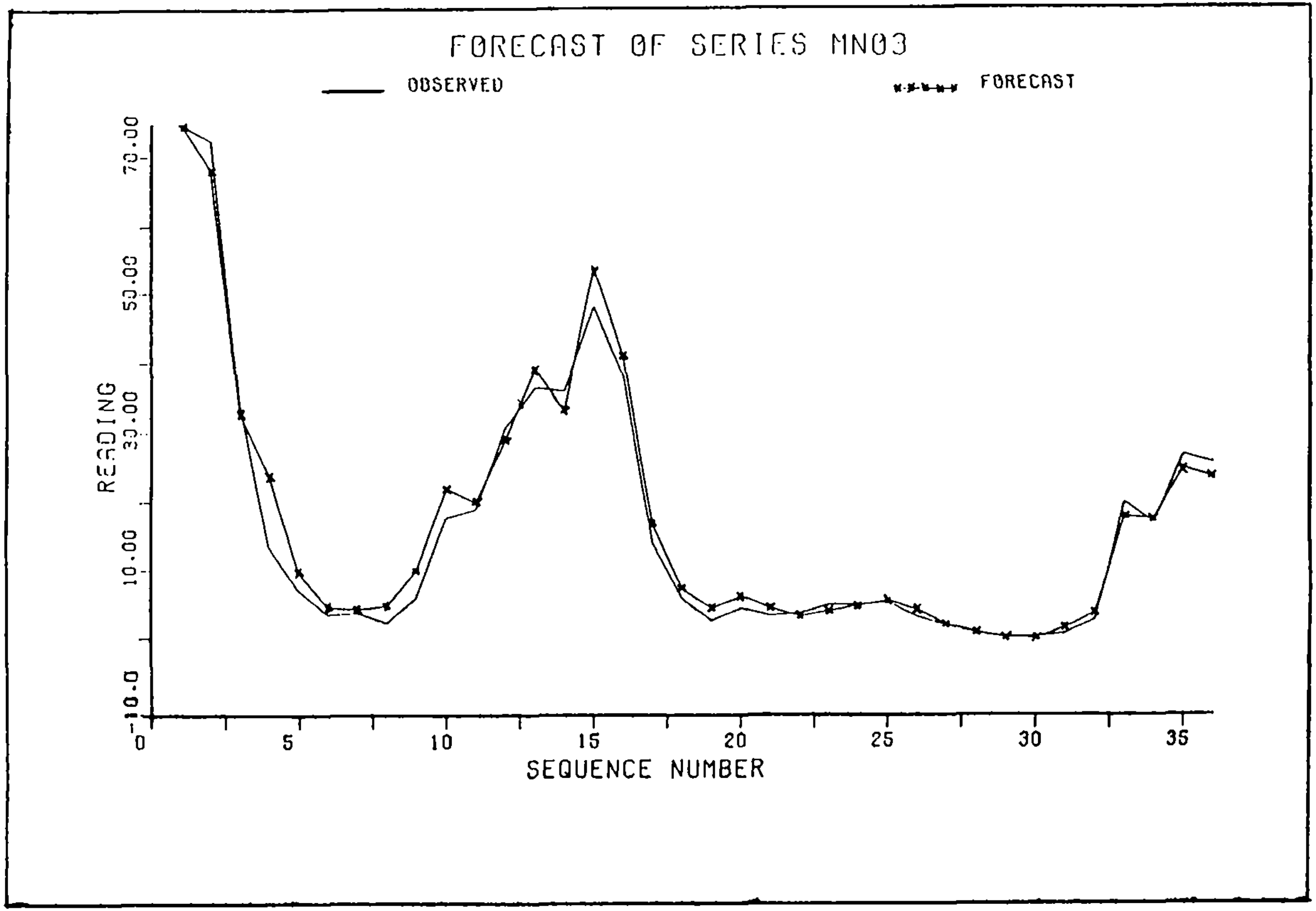

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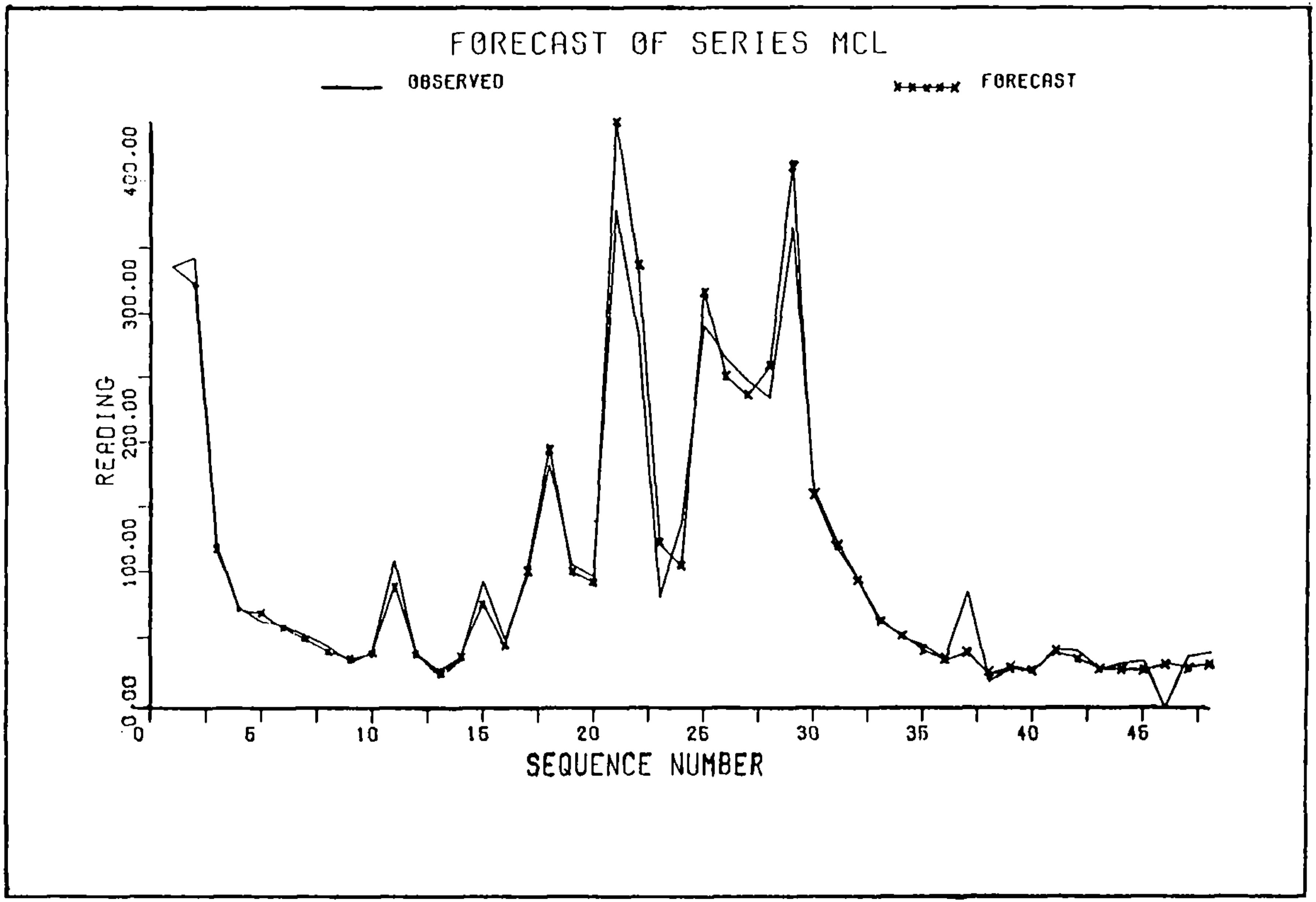

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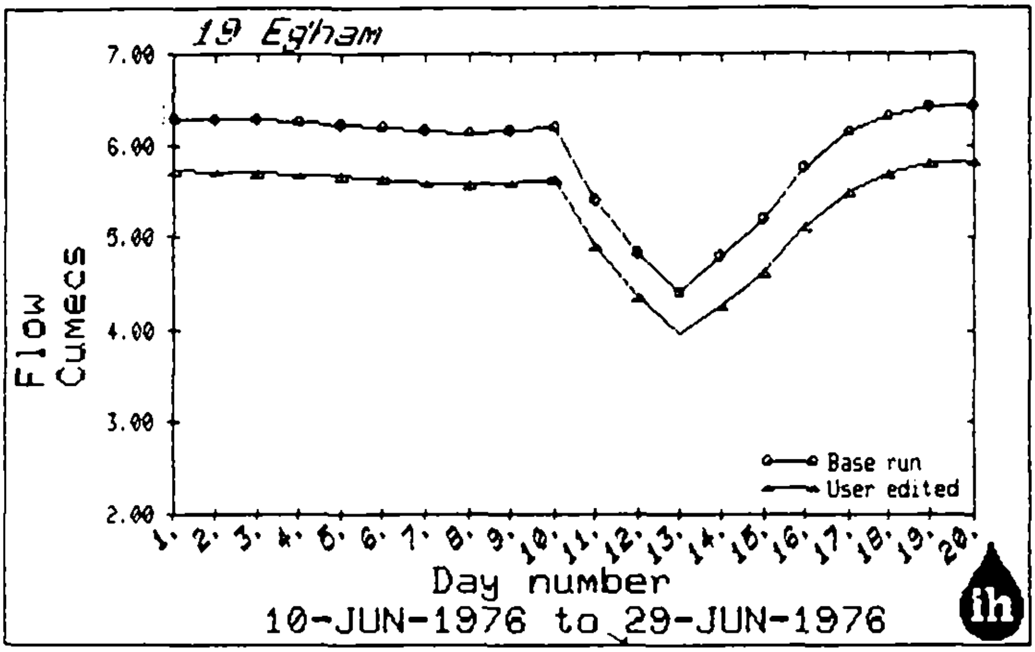

Figure 4.1

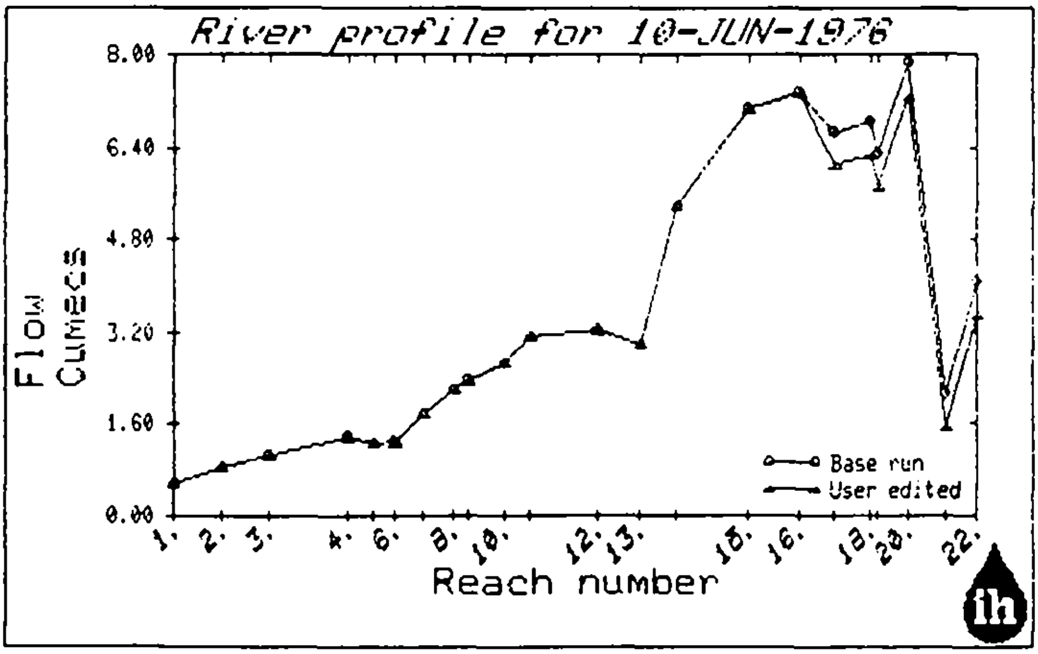

Figure 4.2

to 5 cumecs and this fall might affect navigation in the reach. It would be possible to incorporate flow-level relationships so that levels could be plotted in the same manner. However these relationships will depend on the operation of locks and weirs and must await development by TWA. The effect on flow at all sites on the Thames is shown in Figure 4.2. The profile along the Thames is presented and shows the changes in flow below reach 17. A plot of this profile for the lower reaches of the Thames, Figure 4.3, shows the problems of very low flows at Molesey Weir where a minimum flow of 1.5 cumecs is reached. The effect of the Hogsmill and Mole rivers below Molesey is to increase flows over Teddington Weir (site 22).

4.2 Effects of changing Effluent Flow Rate or Quality

The effects of changing the effluent discharge at Henley has been investigated by increasing the effluent flow by 0.6 cumecs.

The increased load of BOD, nitrate, chloride and ammonia is reflected in the increased concentrations downstream of reach 14 as shown in Figures 4.4, 4.5, 4.6 and 4.7 respectively. The reductions of DO downstream of the discharge is also shown in Figure 4.8. Because many of these variables are non-conservative they change as the water moves down the river. Thus BOD reaches a peak below the effluent discharge but gradually falls as the water moves downstream. Similarly the increased levels of ammonia fall downstream as nitrification processes occur. In the case of dissolved oxygen the initial impact of the effluent is to reduce oxygen levels but these recover downstream as reaeration occurs.

Thus the model can be used to investigate flow and quality changes and could be adopted to other variables of interest to TWA.

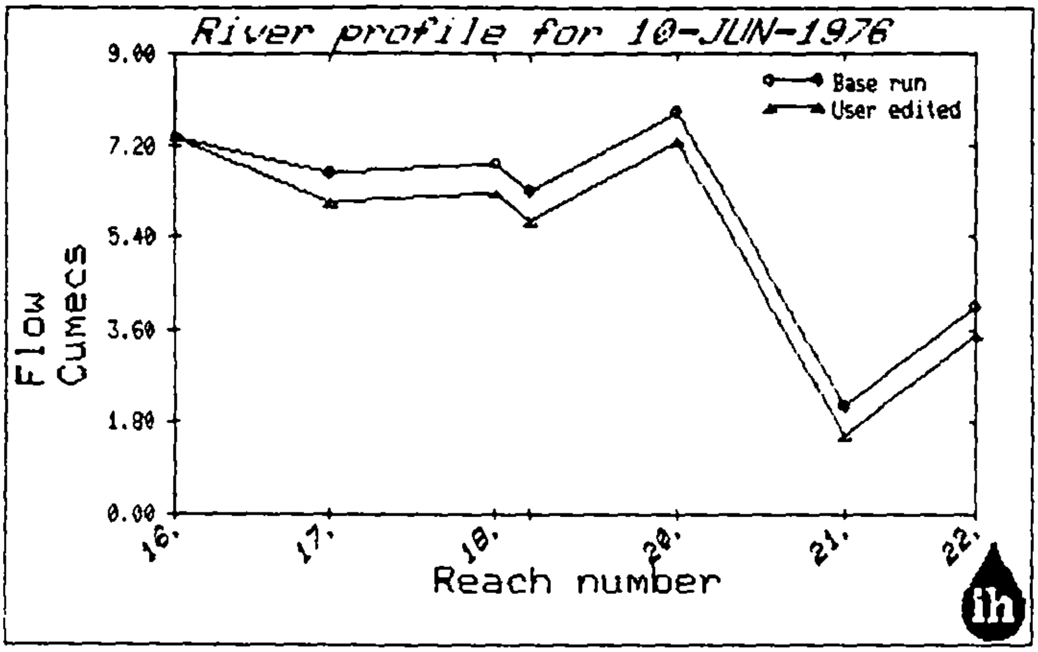
River profile for 10-JUN-1976
9.00
7.20
5.40
3.60
1.80
0.00
Flow
Cumecs
Base run
User edited
16.
17.
18.
20.
21.
22.
Reach number
ih

Figure 4.3

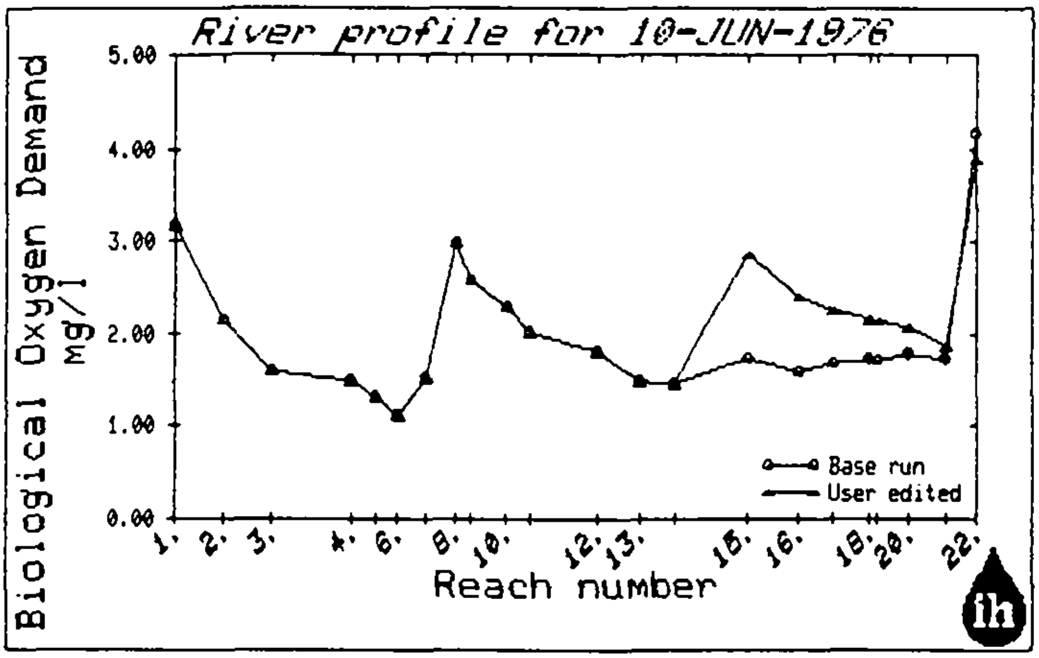

Figure 4.4

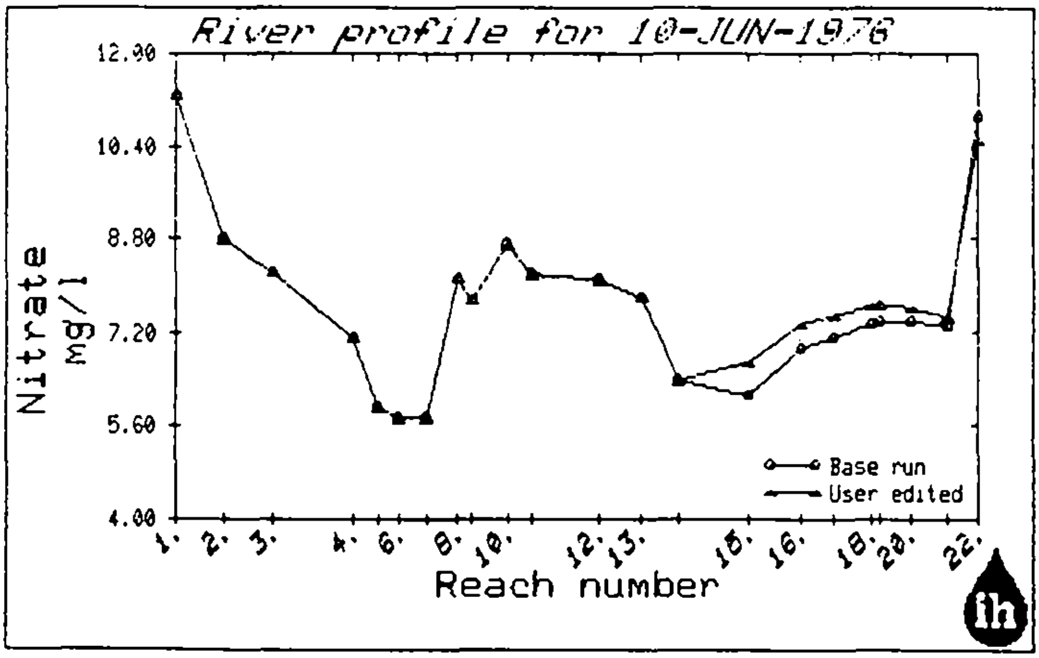

Figure 4.5

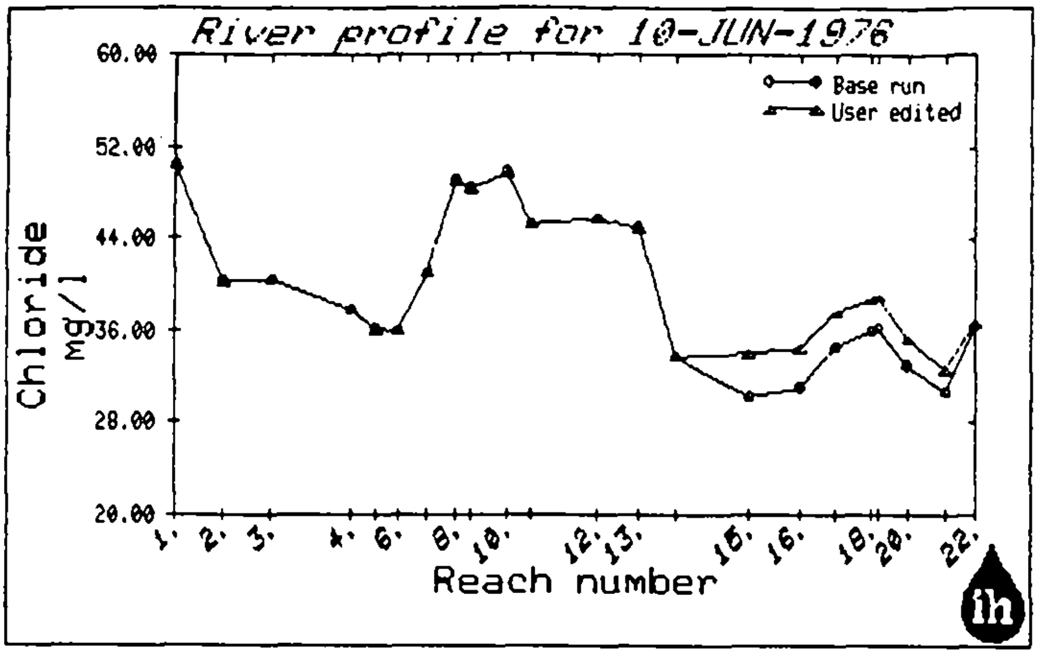

Figure 4.6

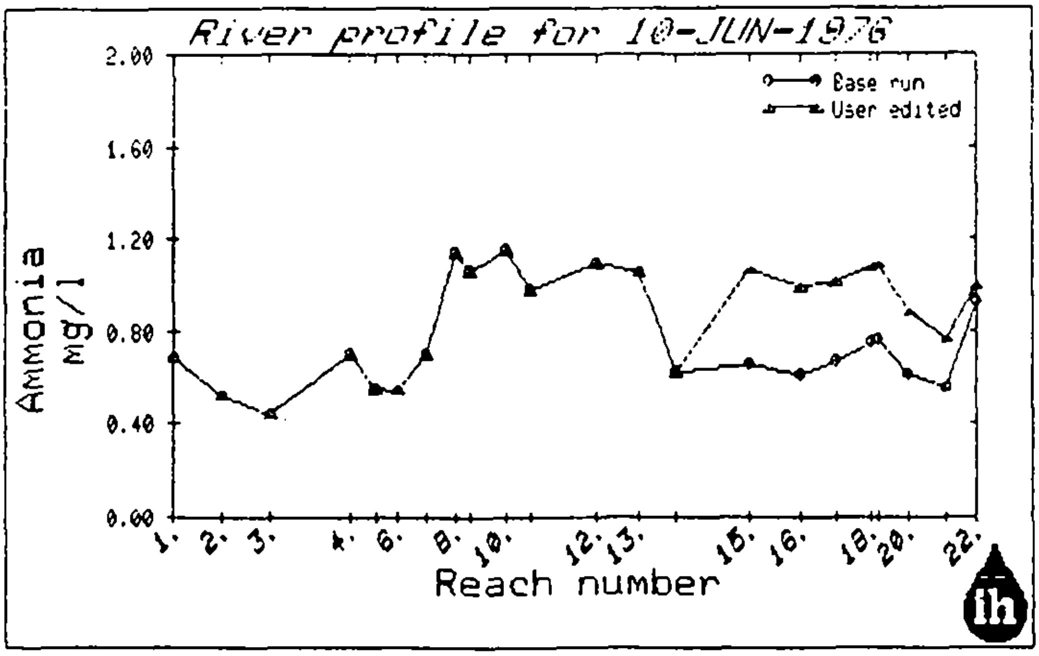

Figure 4.7

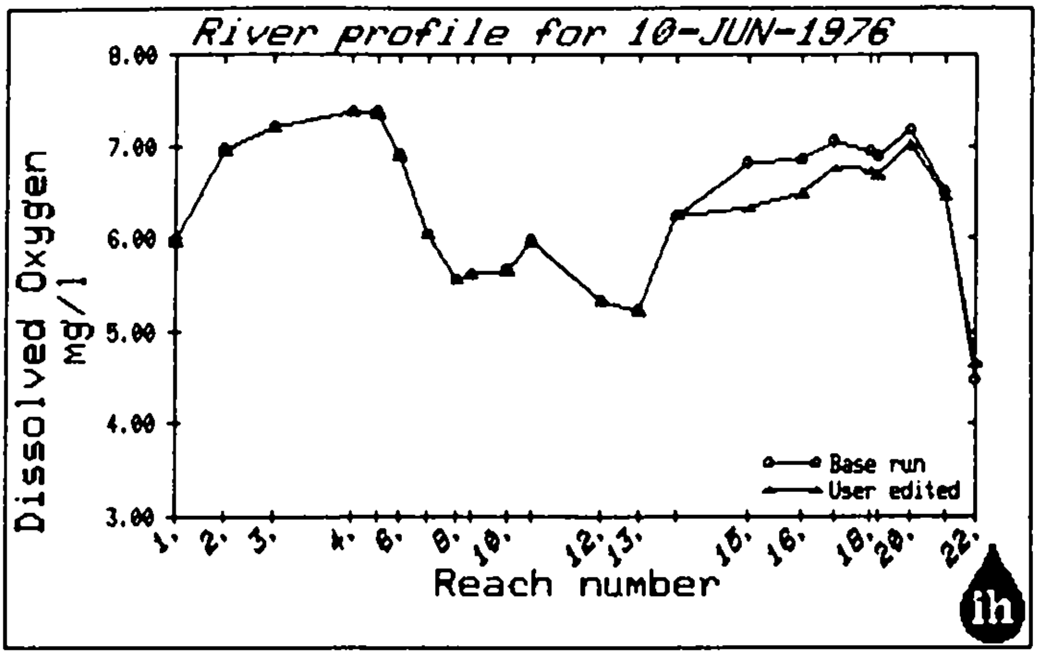
River profile for 10-JUN-1976
Dissolved Oxygen mg/l
8.00
7.00
6.00
5.00
4.00
3.00
1.
2.
3.
4.
6.
8.
10.
12.
13.
15.
16.
18.
20.
22.
Reach number
Base run
User edited
ih

Figure 4.8

5 THE NITRATES PROBLEM

A Nitrates Study of the Thames River Basin

Despite the general improvement in the quality of river water over the past few years, a number of water authorities in the United Kingdom are experiencing difficulties in meeting the CEC standard for nitrate in drinking water. Present trends are not encouraging; nitrate levels in the Thames and the Lea have been increasing steadily over the past 50 years and it is disturbing to note that levels are increasing at an accelerated rate, as indicated in Figure 5.1. In a study of the nitrogen problem in the Thames basin (Onstad and Blake, 1979) it was shown that agricultural inputs

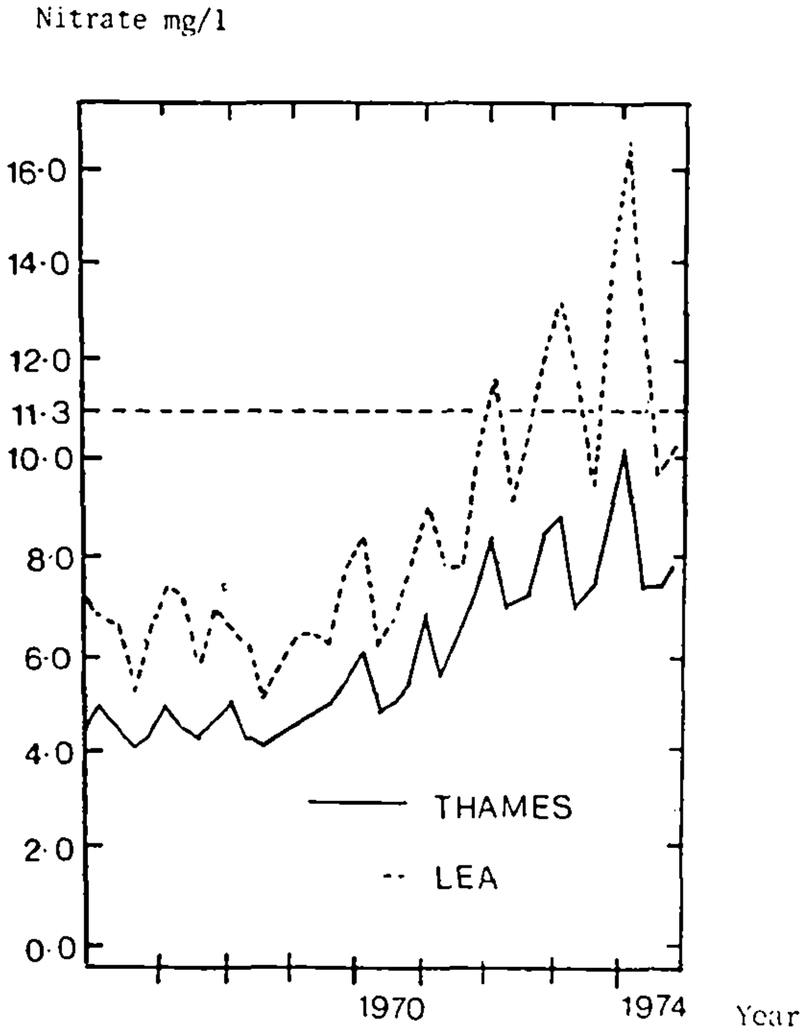

Figure 5.1 Annual nitrate variations for the rivers Thames and Lea.

account for 78% of the variance of nitrogen in the river. Soil nitrate reaches watercourses by two paths, namely a rapid path through the upper soil layer and a slower path through the underlying aquifers, with the lags associated with the aquifer movement of the order of several years. The major factors affecting the agricultural sources of nitrogen were shown by Onstad and Blake to be the release of soil nitrogen in the 1930 - 1940 period after the increased ploughing of grassland and the increased fertiliser applications from the early 1960's.

Onstad and Blake have predicted that by the end of the century the mean concentrations in the River Thames will range from 10 mg N/ℓ to 15 mg N/ℓ for several weeks at certain times of the year. Until now it has been possible to abstract water when concentrations fall below 11.3 mg N/ℓ but this practice clearly cannot be extended for long periods, especially since there is little spare capacity in London's water supply system at present. In addition water demand in London is increasing and the nitrate concentrations therefore pose a significant constraint on water utilization in the future.

As a result of the conclusions drawn by Onstad and Blake the Thames Water Authority needed to evaluate various strategies for managing its present and future water resource system particularly in respect of nitrate concentration.

As an aid to evaluation the Thames Water Authority decided that it had a requirement for a mathematical model to describe the movement of nitrates within the Thames catchment. As a result of this requirement a collaborative study was set up involving the Institute of Hydrology, the Water Research Centre and the Thames Water Authority. Interactions between the different components of the water resource system meant that the overall design model would comprise a number of sub-models representing soil zones, aquifers, treatment works and reservoirs linked together with a main river system model. Thames Water Authority developed models for the reservoir and treatment works and the Water Research Centre provided models describing the groundwater and soil zones. The river model linking all the sub-models together was developed by the Institute of Hydrology (Whitehead et al, 1983). The component parts of the model have all been assembled on the Thames Water Authority computer and it has been used to investigate the nitrate problem given different agricultural strategies.

Application of the Thames Nitrate Model

The model was used to determine the possible implications for nitrate concentrations at two major abstraction sites if no change was made to the water resources system and agricultural land use was allowed to continue on its present course. The Thames Water Authority applied the model to 56 years of hydrological data to reproduce river flows and nitrate concentrations at Farmoor and Datchet which are abstraction sites providing drinking water for Oxford and London respectively. The model was run assuming two sets of conditions:

(a) 1982 agricultural land use, fertiliser application rates, population levels and water demands;

(b) 2006 agricultural land use, fertiliser application rates, population levels and water demands.

The 1982 conditions were based on published land use information and fertiliser surveys and inputs from the sewage treatment plants were based on historical population and per capita consumption data. Forecasts for the 2006 conditions were made from trends in the historical data and estimates of population growth.

The results from the model runs under the two sets of conditions are summarised in Tables 5.1 and 5.2, which show the number of years the WHO limit of 11.3 mg/ℓ would be exceeded at the two abstraction sites considered. It is clear that at both abstraction sites there will be a marked increase in the number of years that 11.3 mg/ℓ would be exceeded if nothing were to be done to control the nitrate problem. It is interesting to note that although the number of years with exceedance is greater at Farmoor than Datchet in 1982, in 2006 the numbers of years of exceedance is similar, at the two sites. This may be because the nitrate load on the

Simulated Nitrate Concentrations for 56-year Hydrological Sample

TABLE 5.1 OXFORD INTAKE ON RIVER THAMES

Duration of exceedance	No. years 11.3 mg N/ℓ exceeded (October - September)	
	1982 land use, population and demand	2006 land use, population and demand
1-15 days	7	10
16-30 days	3	6
31-45 days	2	2
46-60 days	0	1
61-75 days	0	3
76-90 days	0	0
> 90 days	0	0
as annual average	0	0
Total no. years in which exceedence	12	22

TABLE 5.2 LONDON INTAKE ON RIVER THAMES

Duration of exceedance	No. years 11.3 mg N/ℓ exceeded (October - September)	
	1982 land use, population and demand	2006 land use, population and demand
1-15 days	5	8
16-30 days	2	9
31-45 days	0	2
46-60 days	0	1
61-75 days	0	0
76-90 days	0	0
> 90 days	0	0
as annual average	0	0
Total no. years in which exceedence	7	20

river downstream of Farmoor has been increased more than upstream by a larger population increase or increased fertiliser applications. Another possible explanation is that a uniform increase in nitrate load over the river has taken place but the natural denitrification processes are no longer able to remove nitrate at a sufficient rate to prevent its accumulation downstream.

The model runs have thus shown that if nothing were to be done then the abstraction of water from the River Thames for public water supply could be severely restricted by the high nitrate concentrations. The Thames Water Authority can combat this increase using a number of different methods and will be able to use the Thames Nitrate Model to assess which will be the most beneficial to ensure a reliable water supply to its customers.

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APPENDIX I. A DO AND BOD MODEL FOR THE RIVER THAMES

A REVIEW OF DO-BOD MODELS FOR RIVER SYSTEMS

In order to support water-borne life, water must contain dissolved oxygen in sufficient quantities and also be largely free from toxic and harmful compounds. The principal aim of most oxygen balance studies is to assess the impact of effluent discharges on water quality and to quantify the extent of biological self-purification.

Biological self-purification is the process by which organic wastes are broken down by the respiration of micro-organisms into stable end products. It is a biochemical oxidation process through which organic wastes are consumed leaving behind end products such as carbon dioxide, water phosphates and nitrates. The water is 'purified' in the sense that the concentration of waste material has been reduced. Organic materials which can be broken down (i.e. are biodegradable) include natural materials such as simple sugars, starch, fats, proteins as well as more complex natural or synthetic compounds which are found in sewage or other wastes.

The interaction between BOD and DO downstream of a discharge may be illustrated in a simple manner as shown in Figure 1. A high initial BOD exerts a large demand for oxygen and as the instream organic matter decays the oxygen level becomes depressed. The river, however, has the capacity to recover naturally from this situation by the transfer of oxygen from the atmosphere to the water. This process of re-aeration is enhanced by low temperatures and a large degree of turbulence in the river but is primarily controlled by the difference between the saturated oxygen level and the actual river oxygen level. At the minimum of the oxygen sag curve a high level of re-aeration occurs and as the BOD level declines the DO level increases. The minimum is influenced by various factors including the type of effluent and the rate of discharge, a higher organic load producing a lower minimum. In addition, at high river flows the location of the minimum shifts downstream and an important aspect of any water quality study is therefore a satisfactory streamflow model.

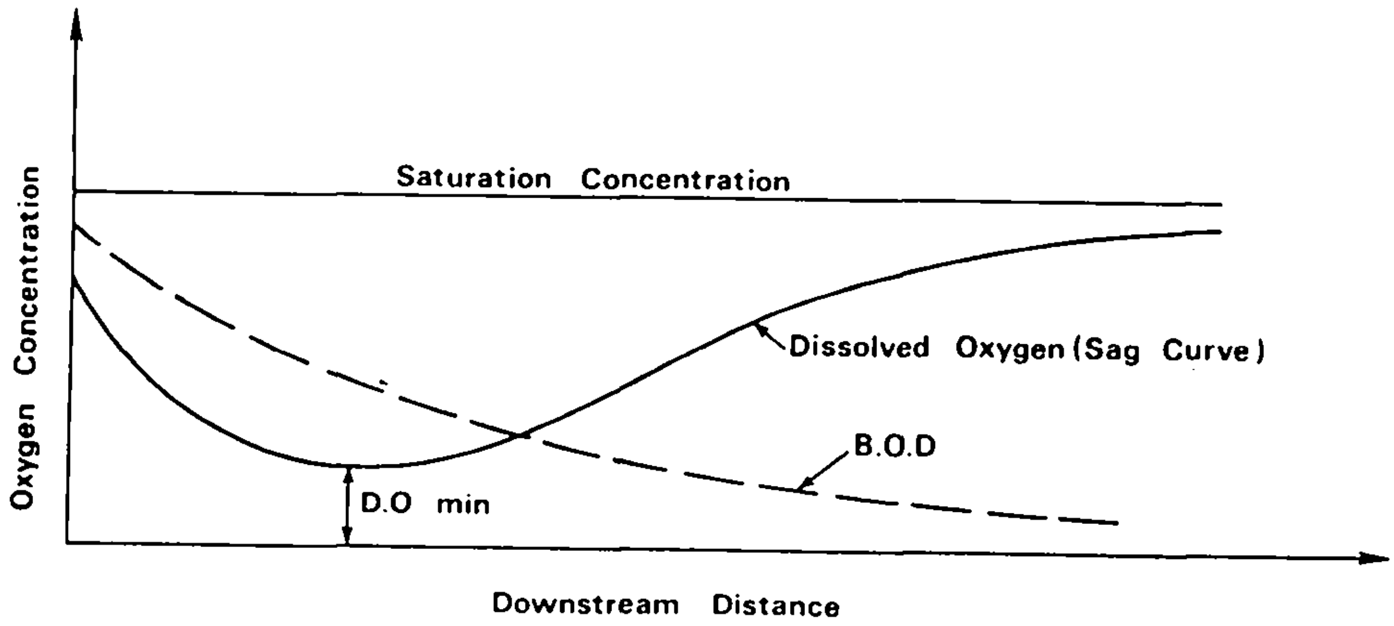

Figure 1. The dissolved oxygen sag curve

All of these processes affect the distribution of DO and may therefore need to be considered in a water quality study. A comprehensive review of the mechanistic terms and model variations is given by Beck (1978) and, as emphasised by Beck, these modifications have in the main been applied to the Streeter-Phelps equations; equations that provide a steady state profile along the stream length.

The steady state model is not, however, particularly well suited to the Thames DO-BOD study. This is because the river is rarely, if ever, in steady state. Flows and, thereby, river velocities change significantly from day to day, as do a number of other variables, such as temperature and solar radiation levels. A dynamic model is required that is capable of accepting time varying inputs and operating upon them to give time varying output responses. Only by comparing the dynamic responses of the DO and BOD behaviour can a realistic assessment of the proposed operating strategies be made.

One possible dynamic characterisation of water quality that appears, on a priori considerations, well suited to this kind of problem, consists of a lumped parameter differential equation model obtained from a mass balance over each reach of the river. The reach is assumed to be uniform throughout and analogous in chemical engineering terms to a continuous stirred tank reactor (CSTR) in which the output concentrations are equal to those in reach. This approach has been applied by Beck (1978) over a single reach of the River Cam in South East England and by Whitehead et al (1981) over several reaches in the Bedford Ouse. The dynamic model resulting from the mass balance is of the following form:-

$$\text{DO:} \quad \frac{dx_1(t)}{dt} = -\left(k_1 + \frac{Q}{V_m}\right)x_1(t) - k_2x_2(t) + \frac{Q\,C(t)}{V_m} + k_1C_s + D_B \qquad (3)$$

$$\text{BOD:} \quad \frac{dx_2(t)}{dt} = -\left(k_2 + \frac{Q}{V_m}\right)x_2(t) + \frac{Q\,L(t)}{V_m} + L_A \qquad (4)$$

where:-

x_1 is the output (i.e. downstream) DO in mg l^{-1}
x_2 is the output BOD in mg l^{-1}
L is the input (i.e. upstream) BOD in mg l^{-1}
C is the input DO in mg l^{-1}
C_s is the saturation concentration of DO in mg l^{-1}
Q is the volumetric flow rate in m^3 days^{-1}
V_m is the mean volume of water held in the reach in m^3
k_1 is the reaeration rate constant days $^{-1}$
k_2 is the BOD decay rate constant days $^{-1}$
L_A is the mean rate of addition of BOD to the reach by local runoff in mg l^{-1} day^{-1}
D_B is the net rate of addition of DO to the reach by the combined effects of photosyntheses, respiration and mud deposits in mg l^{-1}day^{-1}
is time in days

The saturation concentration for DO is determined as,
$C_s = 14.652 - 0.41022T + 0.0079910\ T^2 - 0.000077774\ T^3$
where T is the stream temperature °C.

A common problem with water quality models is to determine parameter values such as the BOD decay coefficient and reaeration rate coefficients. Th standard approach is to select parameter values from the literature or from experimental measurements. Knowles and Wakeford (1978) describe a number of relationships and parameter values which can be used in situations where little information is available and this approach has been applied by Casapieri et al (1978) in a study of the Blackwater Catchment of the Thames.

A more sophisticated approach was developed by Beck and Young (1976) in which the parameters of a dynamic water quality model were estimated directly from field data using the extended Kalman filter (EKF). The EKF is essentially a statistical technique which accounts for measurement errors and system noise both of which are highly significant in water quality studies. Whitehead (1978, 80, 81) applied the EKF technique and the instrumental variable (IV) technique to estimate water quality parameters in the dynamic models developed for the Bedford Ouse. However, a requirement of these techniques is that an extensive record of daily or continuous data is available. In the case of the Cam study, 80 days of data were available and in the case of the Bedford

Ouse over two years of daily data were analysed. In both studies the estimation techniques proved to be extremely useful in identifying model structures and determining model parameters.

In the River Thames study daily data have not been available for such sophisticated analysis and therefore it has been necessary to make use of existing data and information on processes and parameter values. However, rather than develop a steady state model, the nature of the study demands a dynamic model so that the effect of changes in flow, temperature, solar radiation and algal levels can be incorporated. Similar dynamic models for nitrate and algal growth and transport in the Thames have already been developed using routinely collected water authority data (see Whitehead et al 1982, 84) and the approach is used in the current study of DO-BOD variations.

THE THAMES DO-BOD MODEL

The dynamic DO-BOD model for the River Thames is based on equations (3) and (4) described in the previous section but with modifications to account for additional sources and sinks. In particular, the mass balance model includes the effects of tributaries and effluents entering the system and losses of water via abstractions. Processes describing the addition of DO and BOD via photosynthetic oxygen production and phytoplankton death and decay are included together with losses of DO and BOD via respiration of mud or benthic deposits, respiration of phytoplankton and sedimentation processes. As in equations (3) and (4) reaeration and BOD decay processes are incorporated in the model. The following equations apply for each reach.

$$\text{DO:}\quad \frac{dx_1(t)}{dt} = \frac{Q_i(t)}{V_m} C_i(t) + \frac{Q_e(t)}{V_m} C_e(t) + \frac{O_t(t)}{V_m} C_t(t)$$

$$- \frac{Q_a(t)}{V_m} x_1(t) - \frac{Q_o(t)}{V_m} x_1(t) - k_1 x_2(t)$$

$$+ k_2 \, (C_s(t) - x_1(t) + P - R - M \qquad (5)$$

$$\text{BOD:}\quad \frac{dx_2(t)}{dt} = \frac{Q_i}{V_m} L(t) + \frac{Q_e(t)}{V_m} L(t) + \frac{Q_t(t)}{V_m} L_t(t)$$

$$- \frac{Q_a(t)}{V_m} x_2(t) - \frac{Q_o(t)}{V_m} x_2(t) - (k_1 + k_3)x_2(t)$$

$$+ A \qquad (6)$$

Here subscripts i, e, t, a, o refer to input (upstream), effluent, tributary, abstraction and output (downstream) respectively for the reach.

Parameters k_1, k_2 and k_3 are respectively BOD decay rate, reaeration rate and sedimentation rate parameters (day^{-1}) defined as:-

$k_1 = 0.2*1.047^{(T-20)} days^{-1}$ (Wakeford and Knowles (1978))

where T is temperature °C and 1.047 is a temperature correction term.

$$k_2 = 5.316 \frac{u^{0.67}}{d^{1.85}} 1.024^{(T-20)} day^{-1} \quad \text{(Owens et al (1969))}$$

where u is stream velocity m sec^{-1} and d is reach depth, m

$k_3 = 0.1\ days^{-1}$

C_s in equation (3.8) is the saturation concentration for DO defined as:-

$$C_s = 14.652 - 0.41022T + 0.0079910\ T_2 - 0.000077774\ T^3$$

P in equation (5) refers to the addition of oxygen by photosynthesis of plants and algae. In the Thames the river does not support a large biomass of rooted plants because of both depth and high water turbidity. However, algal blooms in spring, summer and autumn are a common occurrence and these have a considerable effect on DO levels, as discussed in section 3.2. Modelling the photosynthetic production of oxygen by algae has been undertaken by many researchers. Steel (1978) describes in detail the processes controlling oxygen production in reservoirs and similar processes are known to occur in rivers.

Research on the modelling of DO-BOD interactions in a river system has been dominated by the classical model of Streeter and Phelps (1925) where the equations take the form:-

$$\text{DO:} \quad \frac{dD}{dt} = k_1L + k_2D \tag{1}$$

$$\text{BOD:} \quad \frac{dL}{dt} = k_1L \tag{2}$$

where L represents the BOD concentration mg l^{-1}, D represents the DO deficit, where the deficit is determined as the difference between the DO saturation concentration and the DO concentration in the stream, mg l^{-1}. k_1 and k_2 are rate constants describing respectively the BOD decay process and the re-aeration process.

It should be noted that this system of two coupled differential equations does not describe the transient behaviour of the DO at a fixed point in the stream but represents an element of fluid moving downstream at the streamflow velocity; in other words it describes a profile or steady state solution along the stream length. In addition, the equations do not reflect the effects of the aquatic environment on the DO distribution. The magnitude of these effects vary from stream to stream according to the physical, chemical and biological conditions and a number of investigations, such as those of Dobbins (1964), Owens et al (1969), Camp (1965), O'Connor (1967) and Thomann (1972) have extended the basic model to include such phenomena as,

(i) the removal of BOD by sedimentation and adsorption;
(ii) the addition of BOD along the reach by the scour of bottom deposits or by diffusion of partly decomposed organic matter from the benthal (mud) layer into the water above;
(iii) the removal of oxygen from the water by diffusion into the benthal layer to satisfy oxygen demand in the aerobic zone;
(iv) the addition of oxygen by photosynthetic action of algae and fixed plants;
(v) the removal of oxygen by respiration of algae and fixed plants.

Owens et al (1969) considered a simplified model in which oxygen production is related to light intensity and plant biomass or algal levels. Whitehead et al (1981) used a modified version of the Owens model and estimated the relevant parameters for the Bedford Ouse. A similar approach has been adopted for the Thames and the following relationship developed

$$P = \frac{8.6}{10^5} Cl_a{}^{0.79} \; 1.08^{(T-20)}$$

Here Cl_a is the chlorophyll-a concentration mg m^{-3}
I is the solar radiation level watt hours m^{-2} per day. The coefficient 8.6 was determined from a linear regression analysis using as variates the observed oxygen production, obtained from continuous data recorded by TWA and $\frac{1}{10^5} Cl \quad I^{0.79} \; 1.088^{(T-20)}$ obtained for the same period.

R in equation (5) refers to the loss of oxygen via algal respiration. Kowalczewski and Lack (1971) developed a relationship between algal concentration measured as chlorophyll a and respiration rate for the River Thames, where

$$R = (0.14 + 0.013 \, Cl_a) \; 1.08^{(T-20)}$$

and this relationship has been incorporated into the model.

M in equation (5) refers to the respiration of the river bed or mud. There has been considerable research into this process (Edwards and Rolley, 1965) and the following equation has been used,

$$M = \frac{k_4}{d} x_1{}^{0.45} \; 1.08^{(T-20)}$$

where x_1 is the DO concentration mg l^{-1}, d is depth, m, and k_4 is a parameter to be determined. The original work of Edward and Rolley was conducted on the highly polluted muds of the River Ivel and later studies by Rolley and Edwards (1967) showed that the parameter k_4 varied considerably from river to river. In the Thames study a value for k_4 of 0.15 days was found to provide the best fit to the observed DO data.

Finally A in equation (6) refers to the conversion of algae to decaying organic matter. In previous algal modelling studies on the Thames (see Whitehead 1984) the concentration of dead algae is assumed proportional to the concentration of live algae. Thus A can be expressed

$$A = k_5 \, Cl_a \, .1.047^{(T-20)}$$

Where Cl is the chlorophyll a concentration mg^{-3} and k_5 is a parameter. From simulation studies on the Thames k_5 was found to be 0.01.

The model has been calibrated using data from TWA routine monitoring sites (NERC Report to TWA, 1984). The DO and BOD model equations have been incorporated into the Thames main stem model and applications are illustrated in section 4.

APENDIX 2

User's guide to the Thames river management system

Kevin B. Black
Institute of Hydrology
August 1984

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APENDIX 2

User's guide to the Thames river management system

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August 1984

CONTENTS

1. Introduction

This document is a preliminary guide for users of the software being developed for the Thames Water Authority.

The software has been written, as far as is possible, in FORTRAN IV under the Digital Equipment Company's RT-11 V5.1 operating system. Some system-dependant software has been written in MACRO 11 assembler where FORTRAN would have been impractical.

2. System considerations

The major hardware requirements for running the Thames software are as follows:

a) One PDP 11/23 processor with 128 Kbytes of memory, EIS and FIS instruction sets.

b) One VT125 Graphics terminal with printer port.

c) One LA50C 80 column dot matrix printer.

d) Dual RL02 10.4 Mbyte removable pack disk drives.

The operational requirements for running the system are as follows:

a) The operating system should be either the RT-11 Single Job or the RT-11 Foreground/Background monitor. Both monitors must be generated to support the virtual memory which is required by the FORTRAN software.

b) The monitor should have at least 44 Kbytes of memory available to the background job. The User Service Routine (USR) may be allowed to swap over the background job to obtain an extra 4 Kbytes for the background job.

c) All logical device name assigments should be disassociated from the physical device names.

d) DL1, which is the RL02 drive where the software resides, should be assigned as the default device.

3. Getting the Thames system started

Under RT-11 a command verb, "THAMES", has been provided. This command has two forms. The first form is :

```
THAMES USER
```

which will assign the Thames disk pack as the default device, set the USR to the swapping state, and deassign all other device assignments. This form is provided for software development.

The second form is :

```
THAMES MENU
```

which has the same effect as the the "THAMES USER" form, but has the additional effect of running a menu program. This program resides at the top of the Thames system structure, and its form will vary in detail as the system is further developed.

4. User interaction with the Thames software

The user interacts with the Thames programs through the keyboard of the VT125 graphics terminal. Most programs are menu and/or form driven. This means that firstly a menu will be displayed offering a choice of actions. The required option may be chosen by pressing an indicated key. For example to select the plot program from the main menu (see section 5.) the user must press the PF4 key. The menu program displays the mnemonic "PF4" in bright reverse video followed by the string " - Plot modelled data", indicating the action this key will initiate. Secondly a form, to be filled in by the user, will be displayed. The form is accompanied by a menu indicating the actions which would be selected as the consequence of typing keys on the keyboard. A user enters data into a form simply by typing. The area available for the data is shown (often by enclosing it in square brackets). If the user attempts to type past the end of the data area then the cursor will wrap around to the beginning of the data area. The data fields within a form contain default values, which the user may edit or leave unchanged.

There are various facilities available to the user when entering data on a form. Any printing character (a printing character is one that you can see on the screen) typed by the user immediately replaces the one currently under the cursor. The cursor then moves over the next character of the data field being edited or to its beginning if it was located on the last character. The user may delete the character to the left of the cursor by pressing the DELETE key. This moves the cursor left one character position and replaces any character there with a blank. If the user attempts to DELETE past the beginning of the data field then the terminal beeper is sounded. The user may move to a selected character within the data field by use of the cursor keys. The left pointing cursor key will move the cursor left one character per depression, and the right cursor key will move it to the right. What happens when the user attempts to move past the beginning or the end of a data field with the cursor keys will be explained later. The user can erase the whole of the current data field by typing the Control and X or the Control and U key combinations (this is achieved, for example for Control and X, by holding down the key labelled CTRL at the bottom left of the main keyboard and typing X). This erases the data field to blanks.

All the form driven programs are written so that if the terminal screen should become corrupted (for example by interference on the mains supply) then it may be restored by typing the Control and W key combination.

Most forms have more than one data field (often of different lengths) displayed to the user for editing. The cursor will always be located on one of these. If the user wishes to alter one of the others then he may do so by moving to it using suitable combinations of the cursor, TAB and RETURN keys. The up and down cursor keys will move the user to the entries immediately above or below the current data field respectively, unless the user is at the top or bottom of the form, in which case the cursor will move to the data field on the bottom or the top of the form respectively. The user may move to the data field to the right (or the one below if there is not one to the right) by pressing the TAB key. The RETURN key has the same effect as the cursor down key.

When the user is at the end of a data field he may move to the data field to the right (or below if there is not one to the right) by pressing the cursor right key. If the cursor is at the beginning of a data field then the cursor left key will move the cursor to a data field to the left (or above if the cursor is on the start of the first data field on the line).

In all cases when the user attempts to move the cursor out of a data field, it is checked for validity. If it is not valid then the terminal's beeper will be sounded and an error message will appear on the bottom of the screen indicating what is wrong.

In all cases when the user presses one of the menu function keys (except when the user is performing a function such as "exit program" when it does not matter) the value will also be checked. The relationships between the values the user has entered will also be checked at this point and if they are incorrect then an appropriate message will appear on the bottom of the screen.

When the user is entering a new value into a form it may be entered in free format. This means, for example, that the user may enter numerical data by entering it at the front of the edit field as if entering it into a calculator. Thus if an edit field for numeric data contained :

```
                  6.500]
```

and the user edited it thus :

```
        [7        6.500]
```

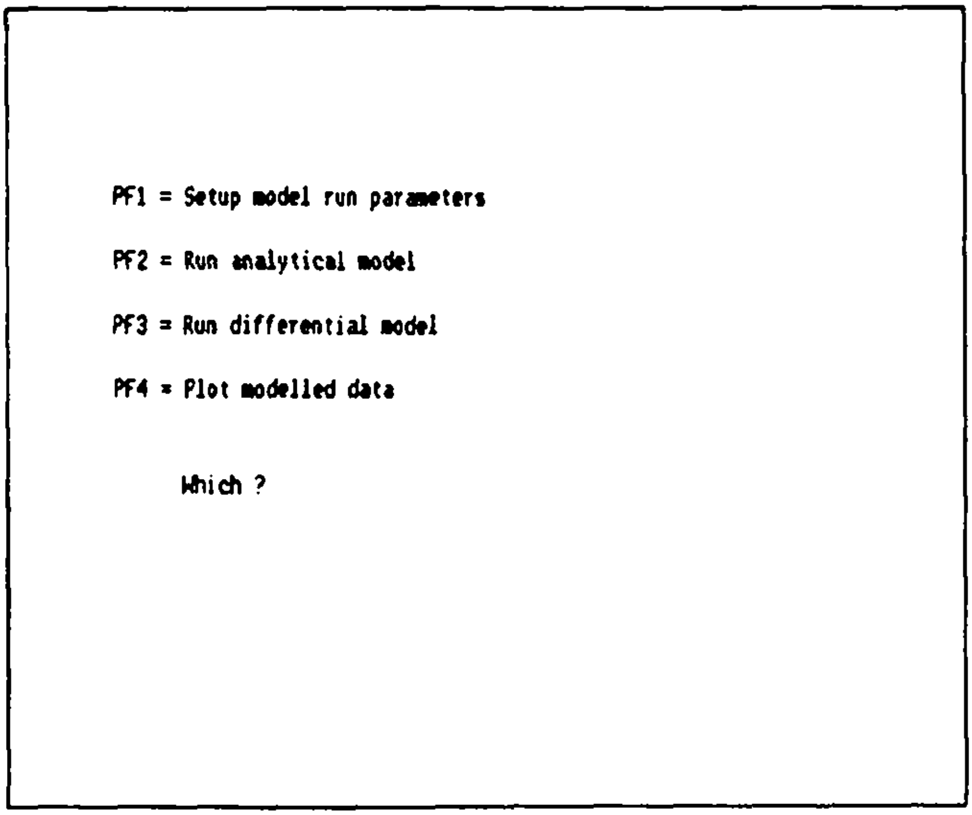
then when the user presses a function key or moves to another edit field, the new value will be inserted thus :

```
                  7.000]
```

The user could also have moved the cursor to the "6" and entered "7.0"; the result would have been the same. A decimal point is assumed to occupy the position of the first blank character after the start of the number if it is not input explicitly).

5. The menu program

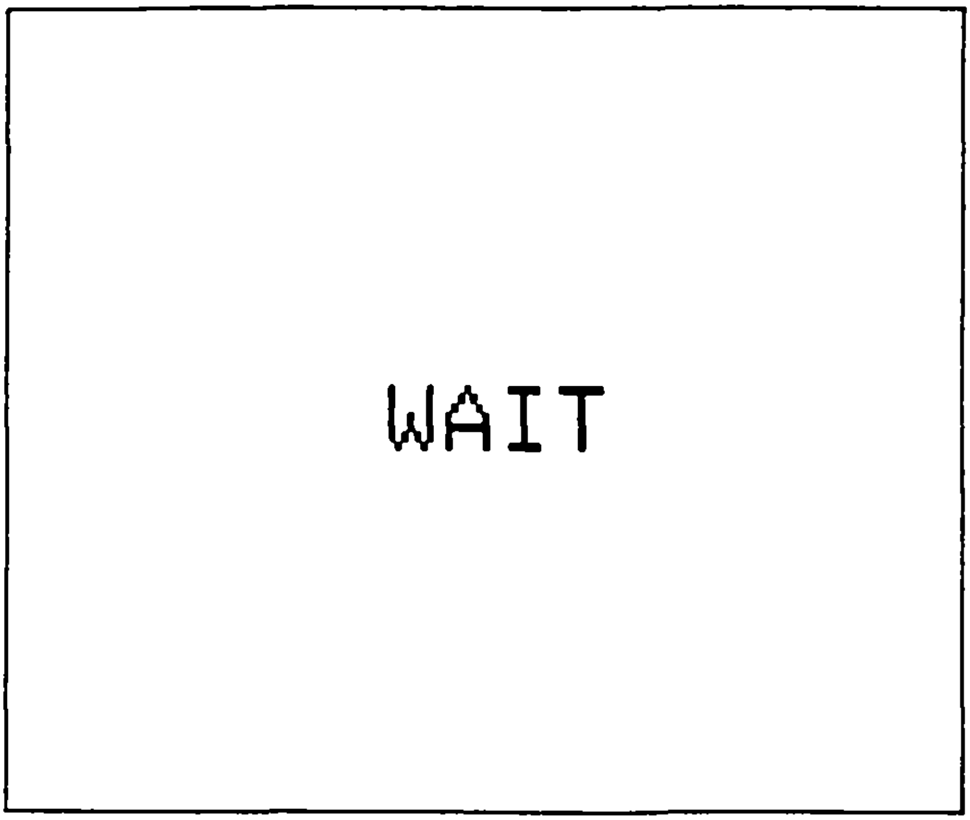
Once the menu program is running the user is provided with a selection of programs which may be run. The screen layout for the menu program is shown in Fig 1. The user may select a program by pressing the appropriate key. For example to run the program which performs the "Plot modelled data" option the user must press the key labelled "PF4", which is to be found at the top of the VT125 auxiliary keyboard which is to the left of the main keyboard.



```
PF1 = Setup model run parameters

PF2 = Run analytical model

PF3 = Run differential model

PF4 = Plot modelled data


        Which ?
```

Fig 1 : The menu program's menu

When the user has pressed a valid key (the terminal beeper is sounded for an incorrect key) a large "WAIT" will appear in the centre of the screen (see Fig 2). The menu program then issues an RT-11 command which will load and run the requested program. The "WAIT" message remains until the selected program has initialized itself and is ready to interact with the user.



WAIT

Fig 2 : The WAIT message

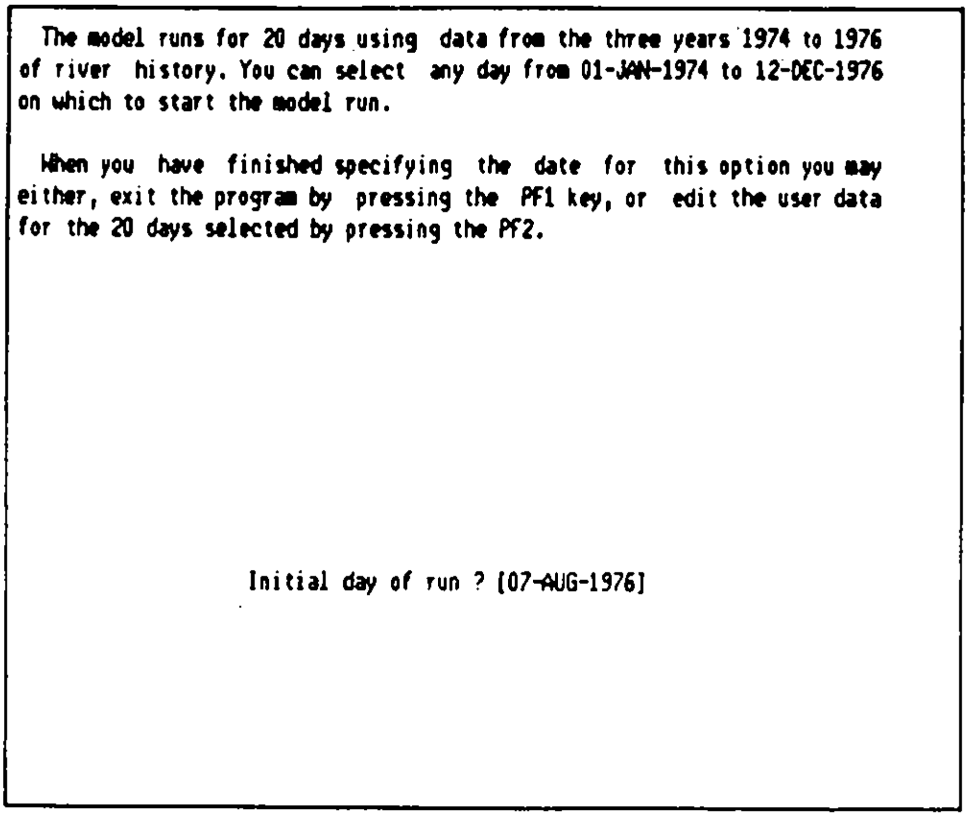
On exit all selectable programs are designed to return to the menu program. However if the program is run from the the RT-11 monitor command level then it will exit to RT-11 with the message "I was not chained to!!". This facility is used to aid program development and debugging.

6

6. Set up model run parameters program

This program is selected from the menu program by pressing the PF1 key. The program allows a user to alter the start date for a model run. It also allows the user to alter the flows and levels of biological oxygen demand at the effluent and abstraction sites down the Thames river.

The first page displayed by this program (see Fig 3) allows the user to select the start date. The start date is restricted by the following factors. Firstly observed data is only available for the three years 1974 to 1976, so the start date must be within one of these years. Secondly the Thames models always run for a 20 day period, so the latest valid day for a model run start is 12-DEC-1976 because there must be at least 11 days of observed data available to the model after the start date.



```
The model runs for 20 days using data from the three years 1974 to 1976
of river history. You can select any day from 01-JAN-1974 to 12-DEC-1976
on which to start the model run.

When you have finished specifying the date for this option you may
either, exit the program by pressing the PF1 key, or edit the user data
for the 20 days selected by pressing the PF2.




                    Initial day of run ? [07-AUG-1976]
```

Fig 3 : First menu in the setup program

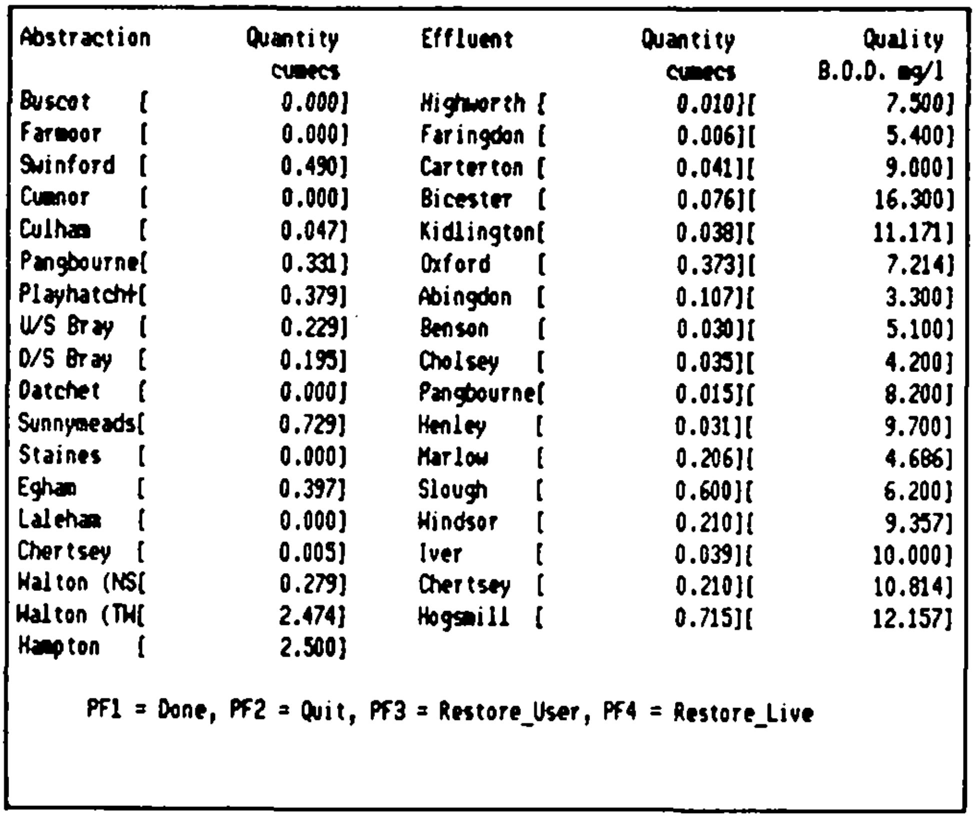
The date is entered in the following form:

"dd-mmm-yyyy"

where "dd" is the day of month, "mmm" the three character month name (from JAN, FEB, MAR, APR, MAY, JUN, JUL, AUG, SEP, OCT, NOV or DEC), and "yyyy" the four digit year number. The "-" characters used to delimit the date may be replaced by any other at the user's convenience.

The function keys PF1 and PF2 may be pressed to either exit the program or to edit/view the flows and biological oxygen demands at the effluent and abstraction sites.

The PF1 key causes the selected date to be stored in the model run file and the program to exit. The PF2 causes the "WAIT" message to appear in the centre of the screen during which the program reads the values of the flow and biological oxygen demand parameters. These are then displayed in table form with the tributary names (see Fig 4). The user may then alter the values as described in section 4. Alternatively one of four actions may be initiated by use of the PF1, PF2, PF3 and PF4 keys.



```
Abstraction       Quantity   Effluent        Quantity        Quality
                   cumecs                     cumecs     B.O.D. mg/l
Buscot     [        0.000]   Highworth [       0.010][         7.500]
Farmoor    [        0.000]   Faringdon [       0.006][         5.400]
Swinford   [        0.490]   Carterton [       0.041][         9.000]
Cumnor     [        0.000]   Bicester  [       0.076][        16.300]
Culham     [        0.047]   Kidlington[       0.038][        11.171]
Pangbourne[         0.331]   Oxford    [       0.373][         7.214]
Playhatch[          0.379]   Abingdon  [       0.107][         3.300]
U/S Bray   [        0.229]   Benson    [       0.030][         5.100]
D/S Bray   [        0.195]   Cholsey   [       0.035][         4.200]
Datchet    [        0.000]   Pangbourne[       0.015][         8.200]
Sunnymeads[         0.729]   Henley    [       0.031][         9.700]
Staines    [        0.000]   Marlow    [       0.206][         4.686]
Egham      [        0.397]   Slough    [       0.600][         6.200]
Laleham    [        0.000]   Windsor   [       0.210][         9.357]
Chertsey   [        0.005]   Iver      [       0.039][        10.000]
Walton (NS[         0.279]   Chertsey  [       0.210][        10.814]
Walton (TW[         2.474]   Hogsmill  [       0.715][        12.157]
Hampton    [        2.500]

     PF1 = Done, PF2 = Quit, PF3 = Restore_User, PF4 = Restore_Live
```

Fig 4 : Abstractions and Effluents flow and quality form

The PF1 key will cause the program to store the displayed flow and biological oxygen demand values in the user file and then returns to the first menu of the program.

The PF2 key causes an immediate return to the first menu of the program. The flow and biological oxygen demand values currently in the user file remain unchanged regardless of what the user may have done to the values that are displayed on the screen.

The PF3 key will cause the program to restore the flow and biological oxygen parameters that the user is editing to those that are held in the user file. Thus if the user incorrectly edits the displayed data they may be restored to the original values.

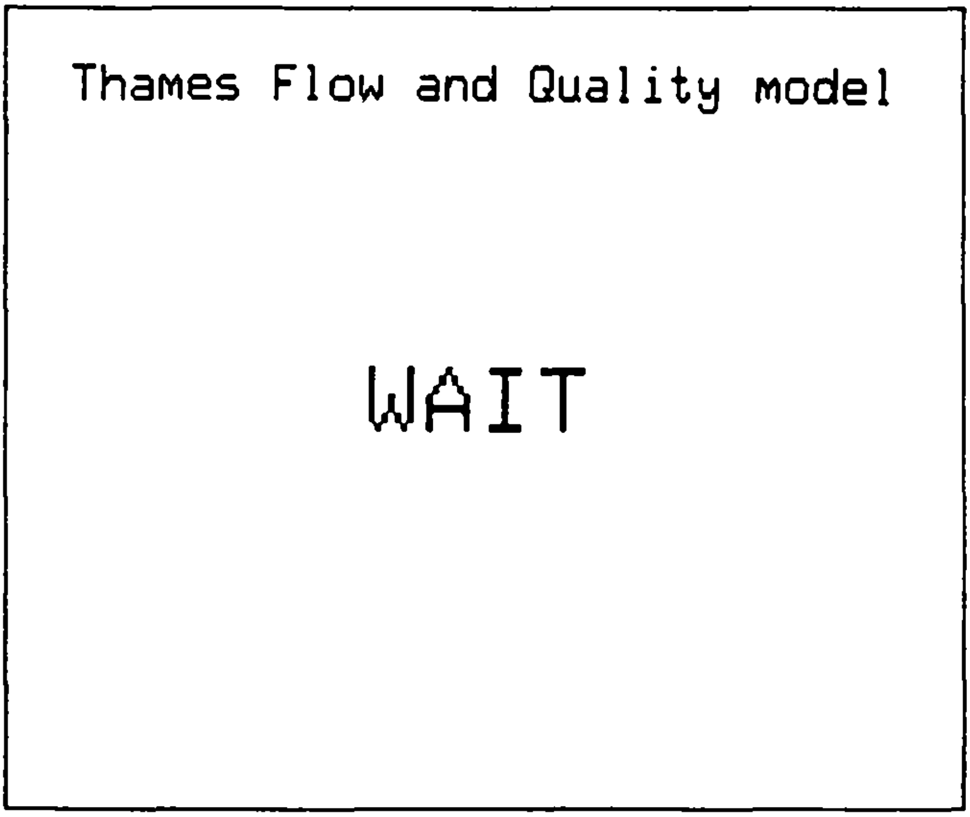
The PF4 key will cause the program to read the flow and biological oxygen demand data from the observed data files and present them to the user for editing into the user file.

7. The model programs

Two model programs are available to the user - the analytical and the differential, selected by the PF2 and PF3 keys respectively. Both models produce two sets of results, one using the observed data and one using the data edited by the user.

The analytical model produces its results by the use of equations derived analytically. The differential model solves a set of differential equations, and typically takes about 6 times as long to run.

When either of the model programs is run it displays the title "Thames flow and quality model" and the "WAIT" message (see Fig 5). No user interaction is involved, and once completed the programs return to the main menu.



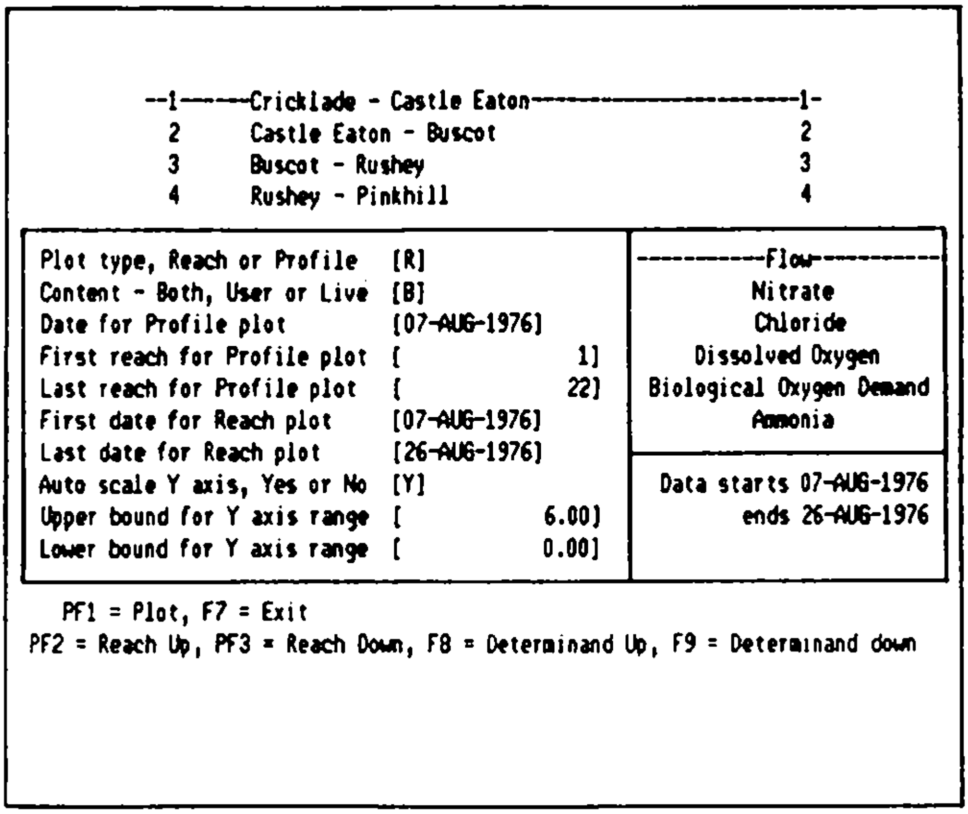
Thames Flow and Quality model

WAIT

Fig 5 : The Thames model message

8. The Plot modelled data program

The plot program presents only one form which allows the user to select the data to be plotted and exercise control over the manner in which it is presented. The form is divided into several areas. An example of the plot form is shown in Fig 6. Two types of plot may be produced; the user chooses whether to produce a Reach or a Profile plot by entering either an "R" for "Reach" or a "P" for "Profile" in the edit field labelled "Plot type, Reach or Profile". Entering any other character in this edit field will cause an error message to appear.



```
      --1-----Cricklade - Castle Eaton--------------------1-
        2     Castle Eaton - Buscot                       2
        3     Buscot - Rushey                             3
        4     Rushey - Pinkhill                           4

 Plot type, Reach or Profile   [R]            |  ----------Flow----------
 Content - Both, User or Live  [B]            |         Nitrate
 Date for Profile plot        [07-AUG-1976]   |         Chloride
 First reach for Profile plot  [          1]  |    Dissolved Oxygen
 Last reach for Profile plot   [         22]  | Biological Oxygen Demand
 First date for Reach plot    [07-AUG-1976]   |         Ammonia
 Last date for Reach plot     [26-AUG-1976]   |
 Auto scale Y axis, Yes or No  [Y]            |  Data starts 07-AUG-1976
 Upper bound for Y axis range  [       6.00]  |         ends 26-AUG-1976
 Lower bound for Y axis range  [       0.00]  |

   PF1 = Plot, F7 = Exit
 PF2 = Reach Up, PF3 = Reach Down, F8 = Determinand Up, F9 = Determinand down
```

Fig 6 : Plot selection form

A "Reach" plot displays modelled data for a user-selected reach for from two to twenty days (also user selected). The top seven lines of the terminal screen are dedicated to the selection of the Reach by the user. There twenty-two major reaches on the Thames, each is held in a list. They are numbered from one to twenty-two. The seven lines displayed are a window on the list. The central line of the seven is displayed in reverse video and names the reach that would be used in a Reach plot. The user may scroll the list up by pressing the PF3 key (this moves the list down river by one reach) - the seven lines scroll up one position losing the top line, an extra line will appear in the seventh position. Alternatively the user may scroll the list down by pressing the PF2 key to produce the reverse effect of pressing the PF3 key. At the top or the bottom of the list (head and tail of river) blank lines are inserted for the non-existent reaches as shown in Fig 6 where the display starts at reach 1 in the central position. If the user attempts to move one of these blank lines into the Reach selection line then an appropriate message appears on the bottom line of the screen. The user can select the range of dates over which the Reach data will be plotted by entering the first and last dates (inclusive) desired in the edit fields labelled "First date for Reach plot" and "Last date for Reach plot" respectively. The format required for entering the dates is as described in the section 6.

The second type of plot is the "Profile" plot. This is a plot of the modelled data for a particular date (user selectable) for a range of reaches (also user selectable). The date for the Profile plot is entered in the form position labelled "Date for Profile plot". The format used is the same as that for the setup program which was described in section 6. The range of reaches to be plotted in the profile are entered in the positions labelled "First Reach for Profile plot" and "Last Reach for Profile plot". Each requires the user enter an integer between one and twenty-two (inclusive). Attempting to enter an invalid number results in an error message. The number entered in the "First Reach for Profile plot" data field must be less than that entered in the "Last Reach for Profile plot", otherwise an error message will appear when the user actually attempts to produce the plot.

Both the models produce two sets of data for each run, one using the observed data and the other for the user edited data. The user can select either or both to be plotted. This is achieved by entering either "B" for "Both data sets", "U" for "User edited data set", or "L" for the "Live (observed) data set" in the field labelled "Content - Both, User or Live". Any other character will cause an error message to appear on the bottom line of the screen.

The models produce data for six determinands (Flow, Nitrate, Chloride, Dissolved Oxygen, Biological Oxygen Demand and Ammonia). The user can select which of these determinands is to be plotted. The names of the six determinands are displayed in a window on the right hand side of the plot editing form (about the middle of the screen). The name of the determinand that is currently selected for plotting is displayed in inverse video. The user may select another determinand by moving either up the list by pressing the F8 key (this is the "8" key on the auxiliary keyboard; note this program distinguishes between the "8" keys on the main and the auxiliary keyboards) or down by pressing the F9 key. The list of determinands does not scroll.

The remaining user control over the plot is the choice of scaling for the Y (determinand) axis of the plot. The scaling may be automatic (values for the lower and upper range are determined by the program) or it may be user specified (the user specifies the lower and upper values of the range). The user chooses automatic scaling of the plot's Y axis by entering "Y" for "Yes" in the edit field labelled "Auto scale Y axis, Yes or No". If the user wishes to specify the lower and upper ranges himself then he must enter "N" for "No" in this field. The values for the upper and lower bounds are then entered in the edit fields labelled "Upper bound for Y axis range" and "Lower bound for Y axis range" respectively. The lower value must be less than the upper value, otherwise when the user attempts to produce the plot an error message will appear on the bottom line of the screen.

Once the user has selected the features desired for the plot he should press the PF1 key. The program then checks that there are no invalid parameters (for example the first Reach to be plotted in a Profile plot being the same or after the last Reach to be plotted). If all parameters required for the type of plot to be produced are valid (those not required for the features selected are ignored) then the screen is cleared, a "WAIT" message appears near the bottom left corner of the screen, and the plot is drawn (this takes about two seconds). Once the plot has been drawn on the screen the "WAIT" message is replaced with a two line menu giving the user two alternatives, either pressing the PF1 key will cause the plot to be copied onto the LA50 printer (if there is one attached to the VT125's printer port). Alternatively the user may press the PF2 key, in which case he is returned to the plot form/menu (which will retain all the selections made by the user before the PF1 key was pressed to produce the plot). An example of the LA50 hard copy output is shown in fig 7.

SECTION 2 - REAL TIME POLLUTION IMPACT ASSESSMENT - THE BEDFORD OUSE STUDY

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AN ON-LINE MONITORING, DATA MANAGEMENT AND FORECASTING SYSTEM FOR THE BEDFORD OUSE RIVER BASIN

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ABSTRACT

Data from Automatic water quality monitors and gauging stations on the Bedford Ouse are telemetered to the Cambridge office of the Great Ouse River Division of the Anglian Water Authority. A mini-computer has been installed to log data from the out-stations, convert data to meaningful units, prepare data summaries, check for alarm conditions and forecast flow and quality up to 80 hours ahead at key locations along the river system. The system provides information on flow and quality conditions in real time and has been used to forecast the movement of pollutants along the river system. A generalised suite of computer programs have been developed for data management and forecasting and a micro-processor controlled water quality monitor is currently under development.

KEYWORDS

Automatic monitoring, pollution forecasting, flow modelling, water quality modelling, data management, telemetry control.

INTRODUCTION

In the management and operational control of water resource systems a major requirement is for information on the present condition of the system and on likely future changes in water quality. Operational managers must be able to respond quickly to emergency situations in order to protect and conserve water quality and maintain adequate water supplies for public use. Moreover, the costs of water treatment and bankside storage are particularly high and there are therefore considerable benefits to be gained from the efficient operational management of river systems from the viewpoint of water quality (Beck, 1981).

In recent years there has been some progress towards providing more efficient operational management by the installation of automatic continuous water quality monitors on river systems. These measure river levels and water quality variables such as dissolved oxygen, ammonia, and temperature and, if combined with a telemetry scheme relaying information to a central location, provide immediate information on the state of the river for pollution officers. Whilst the reliability of such schemes could be better there is now an opportunity to use this information together with mathematical models for making real-time forecasts of water quality.

The practical problems associated with the continuous field measurement and telemetering of water quality have largely limited the application of on-line forecasting and control schemes. The continuous flow of water past sensors for measuring water quality gives rise to severe fouling of optical and membrane surfaces, thereby drastically reducing the accuracy of the data produced. In recent years, however, there have been several studies and applications of continuous water quality monitors (Briggs, 1975; Kohonen et al., 1978). Most UK water authorities have established monitoring and telemetry schemes (Hinge and Stott, 1975; Cooke, 1975; Caddy and Akielan, 1978; Wallwork, 1979) and report reasonable reliability provided the monitors are regularly maintained.

The application of particular interest here is an extensive water quality monitoring and telemetry scheme which has been developed by the Anglian Water Authority along the Bedford Ouse river system in south eastern England. As indicated in Figure 1 automatic water quality monitors have been installed at several sites along the river and data on such variables as dissolved oxygen, pH, ammonia, and temperature are telemetered at regular intervals to the central control station located in Cambridge. This telemetry scheme has been extended to include information on flow and to use a mini-computer located in Cambridge to analyse the data on-line. The system provides rapid information on the present state of the river and incorporates a dynamic water quality model for making real-time forecasts of flow and quality at key locations along the river system (Whitehead et al 1979, 81).

DESCRIPTION OF THE BEDFORD OUSE MONITORING SYSTEM

The Great Ouse basin is one of the largest river catchments in England and is located in the low lying eastern part of the country. It receives one of the lowest annual rainfalls in the country which, combined with a lack of gradient, produces a generally extremely sluggish river.

For simplicity, the Great Ouse basin can be considered as consisting of four sections: the Bedford Ouse, the Ely Ouse, the Middle Level, and the Tidal River. The Bedford Ouse area is the most upstream section of the river and has the highest population density - over 50% of the population in the basin is located in the Bedford Ouse area which represents only 35% of the total area. Figure 2 is a schematic map of the Bedford Ouse area, showing the River Ouse and its major centres of population. As might be expected in a predominantly rural area, there are few large sewage treatment works and very few direct discharges of industrial effluent. Nevertheless, effluent discharges can represent a significant proportion of the river flow under low flow conditions as is demonstrated in Table 1. The table underlines the deteriorating situation in the future due to the expected growth in population of the New City of Milton Keynes. It was largely for this reason, and its associated implications in terms of volumes of water required for public supply and volumes of effluent requiring disposal, that this study has concentrated upon the Bedford Ouse area.

There are three major abstractions for potable supply within the area - at Foxcote, Clapham (Bedford) and Offord; and these are also shown in Figure 2. A further abstraction at Brownshill may be considered in the future as a means of increasing the yield of the public water supply reservoir at Grafham (which is at present supplied by the abstraction at Offord).

FLOW AND WATER QUALITY INSTRUMENTATION AND TELEMETRY

The telemetry scheme used for flow and quality monitoring is a Dynamic Logic TELTEL System, which employs the public switched network (STD) telephone system.

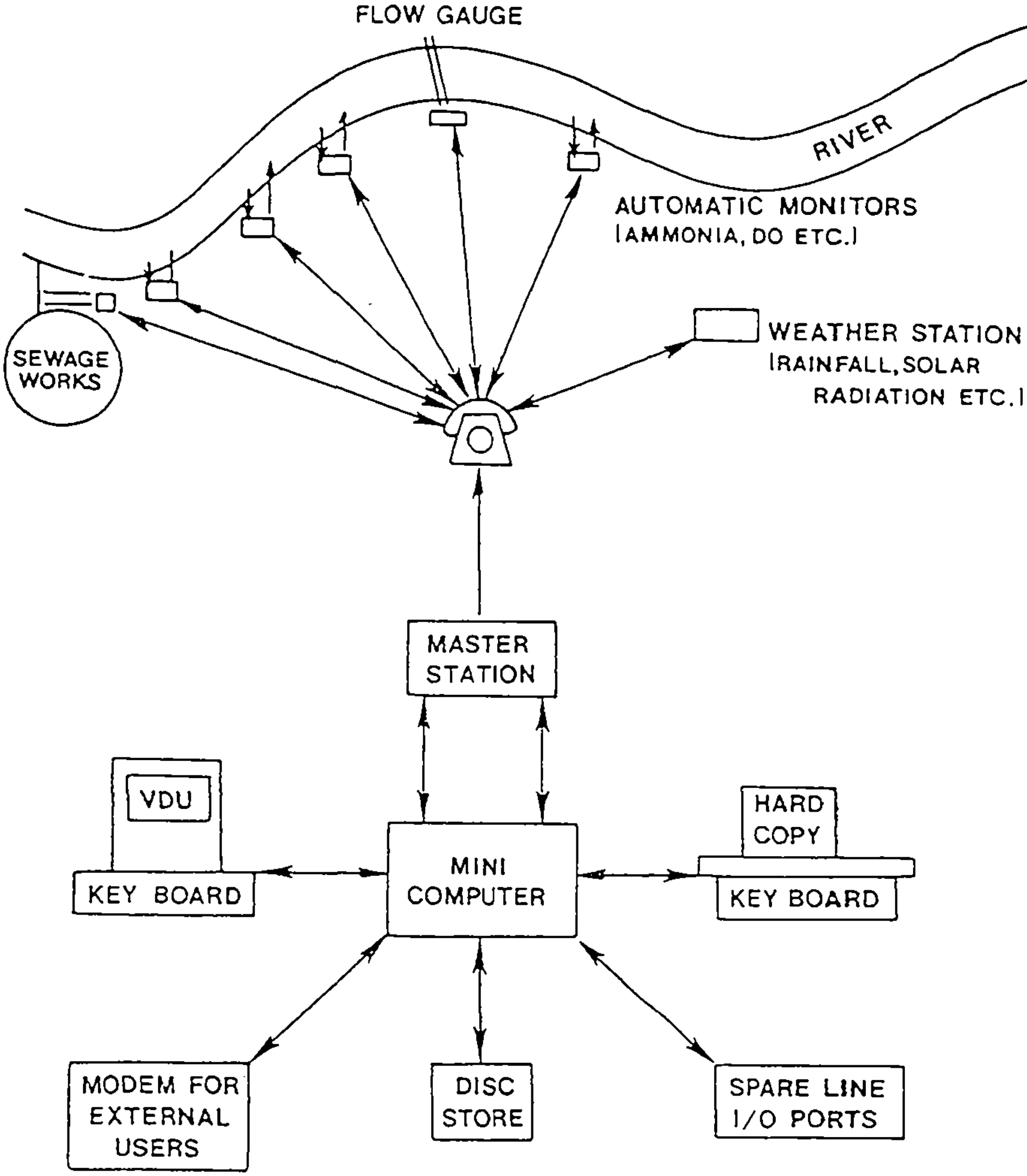

Figure 1 Water Quality Monitoring, Telemetry and Mini-Computer Processing System for the Bedford Ouse.

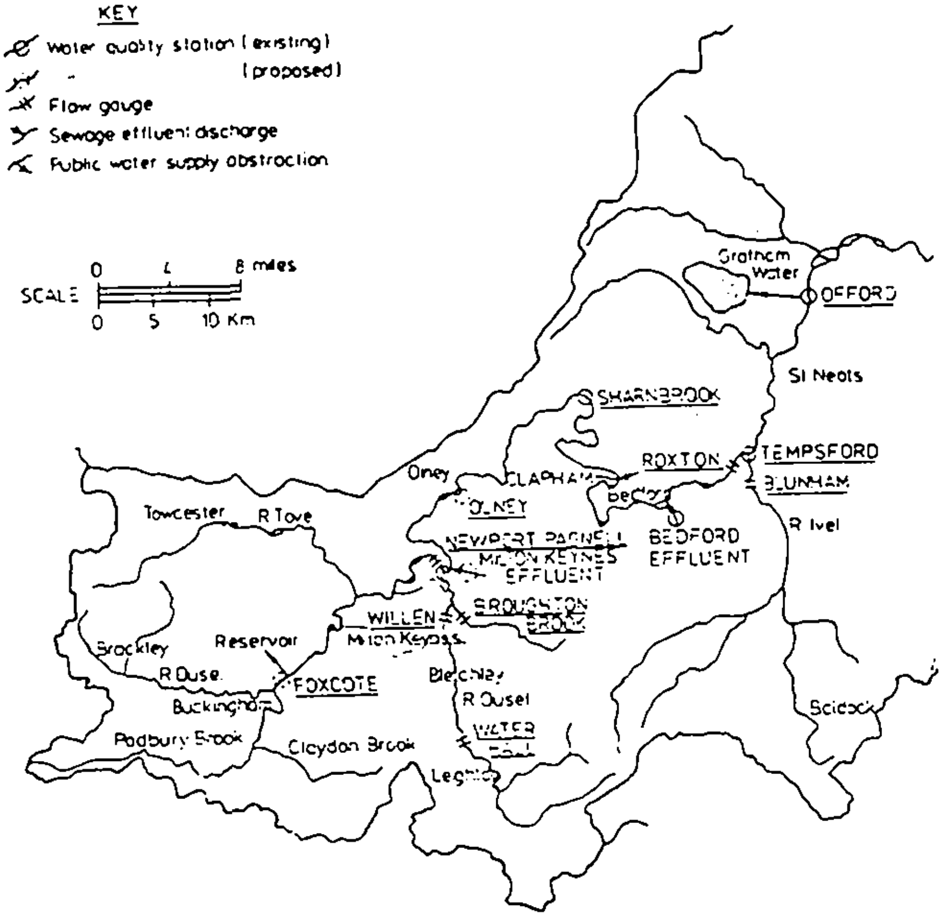

Figure 2 Bedford Ouse System showing the Deployment of Water Quality Monitors and Flow Gauging Stations

Outstations can be interrogated from the Dynamic Logic TELTEL dedicated master station.

TABLE 1 Proportion of Effluent in the R. Ouse

Location (in order downstream)	Percentage of Effluent in Total River Flow		
	1968	1981	2001
Foxcote	20	30	30
Clapham	35	60	70
Offord	45	60	85
Brownshill	25	35	45

Flow stations included in the telemetry scheme are located at the following sites:

(i) Newport Pagnell - River Ouse
(ii) Willen - River Ouzel
(iii) Broughton - Broughton Brook
(iv) Roxton - River Ouse
(v) Blunham - River Ivel

Water quality stations are located at the following sites:

(i) Newport Pagnell - River Ouse and River Ouzel
(ii) Sharnbrook Mill - River Ouse
(iii) Bedford - Sewage Effluent
(iv) Tempsford - River Ouse and River Ivel
(v) Offord - River Ouse
(vi) Barrington - River Rhee
(vii) Bottisham - River Cam

Additional stations are to be installed by the Anglian Water Authority at Buckingham and at Olney, both on the River Ouse.

The monitoring stations use specific ion electrodes for measuring such variables as ammonia and nitrate and standard sensors for measuring dissolved oxygen, conductivity, temperature and pH. In Figure 3, an example of a DO record shows clearly the daily oscillation of dissolved oxygen production and consumption processes and the longer term fluctuations which are due to other variables such as temperature and streamflow.

DESCRIPTION OF MINI-COMPUTER SYSTEM FOR DATA MANAGEMENT

The benefits to be gained from a mini-computer data management system are as follows:

(a) Improved operational management. The system provides real-time (i.e. immediate) information on the quality of the river thus enabling pollution officers to detect pollutions at an early stage and to respond quickly and efficiently;

(b) Dissemination of information. Information on the present quality of the river is available for operational management and daily, weekly and monthly summaries made available for management reports.

(c) Optimisation of capital and revenue expenditure. A significant saving in capital expenditure and in laboratory and other running costs should be possible

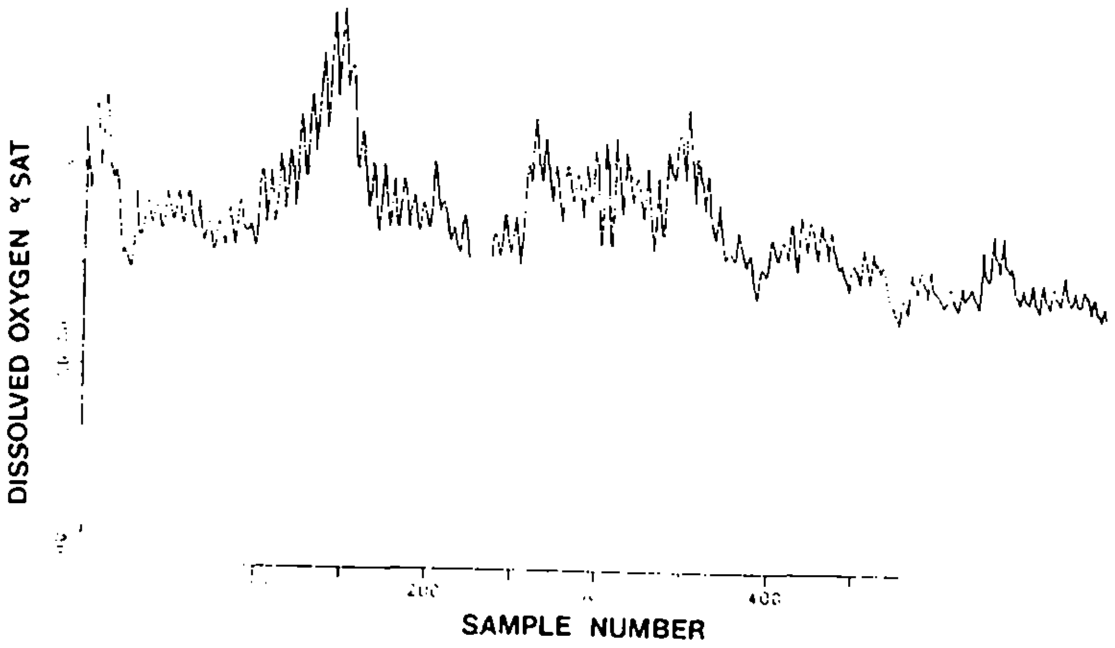

Figure 3 Dissolved oxygen levels on Bedford Ouse (Tempsford Monitor) July to December, 1978, measured at 4 hourly intervals.

by the more efficient operational management of the system. For example, it would be unnecessary to expand the water storage facilities at Bedford (currently 18 hours hold-up time) as a reliable forecast of pollutant loads allows sufficient time to switch in alternative supplies from groundwater or reservoirs. Also savings in operational costs can result if the time of a pollution load can be forecast and treatment such as chlorination increased to match the arrival time rather than increased well in advance of the arrival;

(d) Improved understanding of water quality. Information from the water quality data would improve the understanding of the river system and the effect of water quality on the river ecology;

(e) Accurate predictions of time of travel and dilution factors. Given a model of the river system it is possible to predict the time of travel of a pollution load and the dilution factors along a particular stretch of the river. This assists the pollution inspectorate to assess the significance of pollution under given conditions;

(f) Forecasts of water quality. A model of the system can provide forecasts of key water quality variables (nitrate, dissolved oxygen, ammonia, etc.) at critical points along the river.

The success of the monitoring and forecasting system depends on the reliability of the instrumentation and telemetry hardware and the way in which the data are processed. At the most basic level of analysis it is necessary to convert the instrument signals to meaningful concentration units. With the use of the mini-computer is it possible to make these conversions conveniently and to provide data listings, summaries and graphical output for operational management. On a more sophisticated level the computer can be programmed to forecast water quality conditions using a mathematical model and hence provide advance warning of the effects of pollution events.

In order to meet these requirements a DEC MINC computer system has been installed at the Cambridge office of the Great Ouse Area Office of the Anglian Water Authority. The DEC MINC system incorporates a PDP 1123 (16 Bit) computer with 128k of store, a storage system based on 2 floppy discs (1 Megabyte of store), a visual display screen, together with a keyboard, extensive input-output facilities and a software system capable of supporting a FORTRAN compiler. In addition to the basic system a DEC writer was also required for listing data and a plotter for producing graphical output.

Data are relayed to the centre at Cambridge where equipment is situated for telemetry control, data processing and report production (Figure 1). The scanning of the flow gauges and water quality monitors is computer controlled with the outstation telephone numbers, which are held in computer memory, being fed to the master station (autodialler/receiver). After making contact with an outstation, data are transmitted and checked before being stored in the computer memory for further processing. Information can be presented to operating staff in several forms and data summaries, alarm messages and graphical displays are available on either the printer or on the visual display unit. The computer system can be operated by staff not qualified in computer science and the Institute of Hydrology have devised an interactive system which prompts the user into selecting options which appear on the visual display unit.

An important function of the mini-computer is the storage of data and this is achieved using the two double density floppy discs capable of storing several week's data for all the monitoring stations. Data stored on the floppy discs can be retrieved at any time for direct listing or for the calculation of summary statistics such as daily mean, maximum, minimum and 95 percentiles. The logging program on the micro-computer allows the acquisition of both analogue data (ie measurements from water quality instruments) and digital signals related to equipment status (eg pump failure). Comparison of data with preset alarm levels enables warning messages to be given in the event of a pollution incident. Given such warnings the situation can be investigated using the mathematical model to obtain forecasts of flow and water quality up to 80 hours ahead, given certain assumptions on the upstream conditions during the forecast period.

The options available on the mini-computer system are selected using a simple interactive system by which the operator is prompted to answer questions displayed on the screen. The options available may be summarised as follows:-

Start logging: which allows the operator to start the collection and storage of data from the outstations at predetermined times. The logging program also converts the instrument signals to river flow or concentration units, allows for calibration factors and prints out alarm level messages, equipment status and daily statistics.

Interrogate outstation: which allows the operator to interrogate any outstations of his/her choice immediately. This is particularly useful if a pollution incident has occurred, or when installing and maintaining instruments.

Plot data: which provides the operator with a choice of various graphical presentations of data on the visual display screen. Plots may be obtained for the data collected at any outstation.

Edit master file: which allows the operator to create or edit the masterfile which holds all the fixed parameters describing each outstation's configuration and other attributes such as site name, telephone number, type of instruments, equations defining data conversions, calibration factors, alarm levels and warning messages and equipment reliability.

Print master file: which allows the operator to list the contents of the masterfile on the DEC printer.

Print dial out statistics: which reports the number of successful and failed dail out attempts for each outstation.

Print daily, weekly, monthly and annual summaries: prints the selected summary (mean, maximum, minimum standard deviation, 95 percentile) on the DEC printers (See Table 2).

Run flow and water quality model: asks the system to run the flow and water quality model using data held on disc.

Run impulse model: asks the system to run the impulse model using data supplied by the operator on the type of pollutant (BOD, ammonia or conservative pollutant), pollutant flow rate, concentration and location of discharge.

List station data: prints the output data for a specified station (see Table 3).

The programs for all these options have been written in standard Fortran so that the system can be easily modified as water authority requirements change or can be transferred to other computer systems.

TABLE 2 Summary of daily data (Current data at Barrington on Friday 21 August 1981

Instrument	'n'	Minimum	Maximum	Mean	Standard deviation	95 Per'ile	Units
Dissolved oxygen	7	48.8	105.1	75.9	22.70	113.3	% sat
Temperature	7	14.0	15.5	14.6	0.51	15.5	centigrade
Conductivity	7	869.1	957.0	927.7	33.35	982.7	u siemens
Ammonia (as N)	7	0.04	0.04	0.04	0.00	0.04	(mg/l)
pH	7	7.7	8.3	8.0	0.21	8.3	-

TABLE 3 List of station data (Data logged to date for Barrington on Tuesday 22 September 1981 11-00-39)

Date	Time	Dissolved Oxygen (% saturation)	Temperature (centigrade)	Conductivity (u siemens)	Ammonia (as N) (mg/l)	pH
19.8.81	0900	50.00	15.60	947.21	0.04	7.73
19.8.81	1120	64.06	15.79	966.74	0.04	7.83
19.8.81	1149	66.79	15.79	966.74	0.04	7.86
19.8.81	1216	71.48	15.79	956.97	0.04	7.88
19.8.81	1219	72.26	15.89	956.97	0.04	7.89
19.8.81	1224	73.43	15.89	956.97	0.04	7.89
19.8.81	1234	75.78	15.89	956.97	0.04	7.93
19.8.81	1239	76.95	15.89	956.13	0.04	7.83
19.8.81	1244	76.56	15.89	956.97	0.04	7.99
19.8.81	1249	77.73	15.89	956.97	0.04	7.95

MODELLING FLOW AND WATER QUALITY

The model developed for the Ouse is an operational model and is therefore designed to use time varying input (upstream) measures of flow and water quality to compute time varying output (downstream) responses. The model characterises the short term (hourly) system behaviour and provides a mathematical approximation to the physico-chemical changes occurring in the river system. The structure of the model developed for the Bedford Ouse is shown in Figure 4; a multi-reach flow model is linked with the water quality model so that flow quality interactions are incorporated directly. A detailed description of the flow and quality model is provided elsewhere (Whitehead et al 1980, 81), a summary is included here. The model is based on a twenty reach representation of the Bedford Ouse river, (see Table 4) in which each reach is characterised by a number of compartments. The model for flow variations in each compartment is based on an analogy with the mass balance equations for the variations in concentration of a conservative pollutant under the assumption of uniform mixing over the compartment. Alternatively, the model may be viewed in hydrological flow routing terms as one in which the relationship between inflow I, outflow Q and storage S in each compartment is represented by the equation:

$$\frac{d(KQ)}{dt} = (I - Q) \qquad (1)$$

where K is a travel time or residence time parameter which varies as a function of stream velocity as follows:

$$K = \frac{L}{UN} \tag{2}$$

where N is the number of compartments in the reach, L is the reach length, and U, the mean flow velocity in the reach, is related to discharge through:

$$U = a\,Q^{b} \tag{3}$$

TABLE 4 List of reach boundaries

Reach boundaries	Length of reach (m)
Newport Pagnell	
to	5200
Tyringham Bridge	
to	3000
Ravenstone Weir	
to	4800
Olney Weir	
to	4000
Lavendon Weir	
to	4800
Turvey	
to	5300
Harold Weir	
to	8040
Felmersham	
to	8850
Stafford Bridge	
to	6260
Oakley Weir	
to	3370
Clapham (AWA Absraction)	
to	3220
Bromham Weir	
to	4000
Bell End Weir	
to	5150
Cardington	
to	2080
Castle Mills	
to	3680
Willington	
to	2240
Barford	
to	4320
Roxton	
to	7200
Eaton Socon	
to	4000
St Neots	
to	2080
Offord (AWA Abstraction)	

In order to evaluate the Bedford Ouse velocity-flow relationships, a series of tracer experiments has been conducted on the river. A known mass of iodide was injected into the river and the iodide concentration determined at one or more selected locations downstream either continuously using selective ion detection

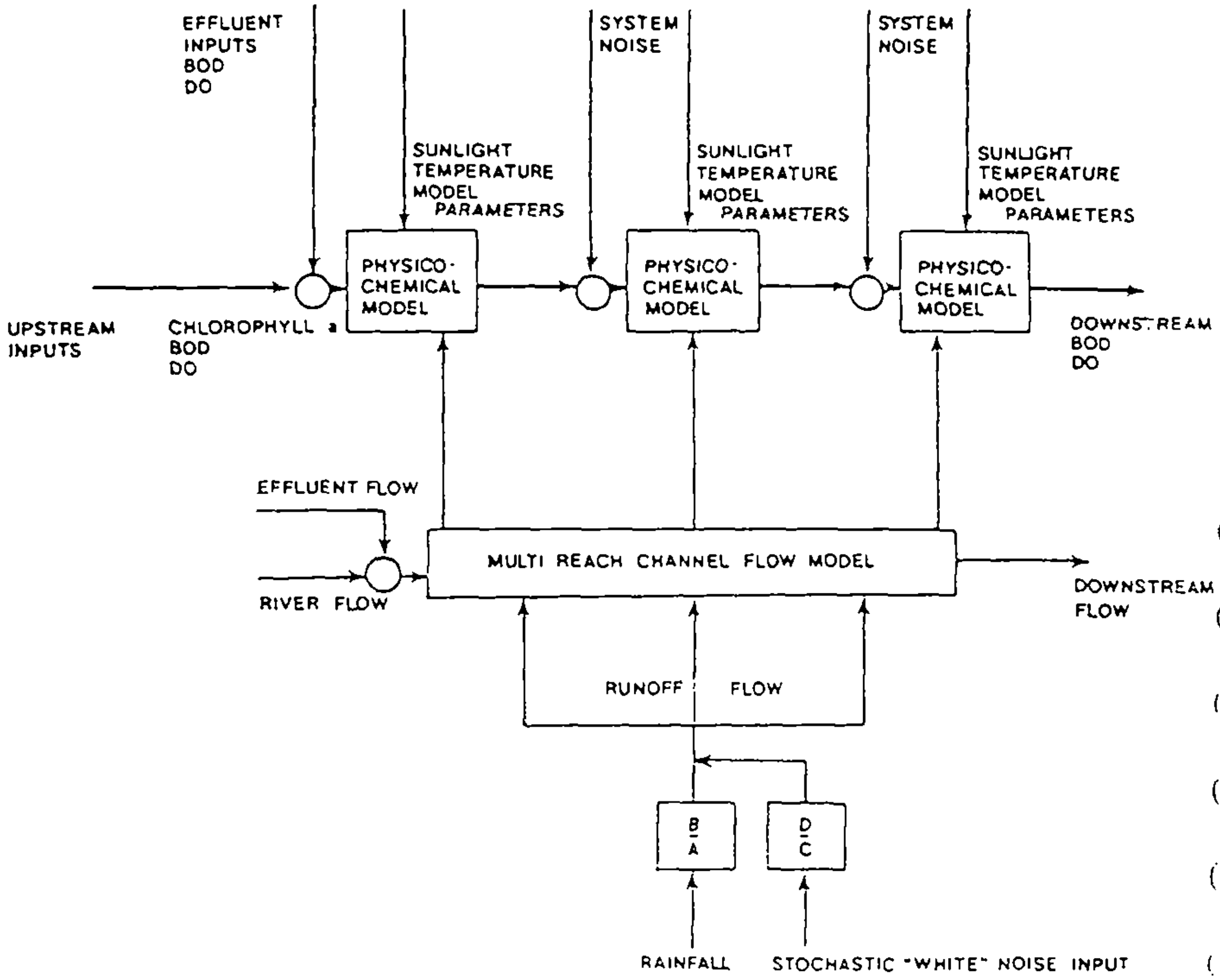

Figure 4 Schematic representation of dynamic flow and water quality model.

equipment or by sampling the river water and subsequent analysis of the samples at the Institute of Hydrology (see Figure 5). Using information on velocity and flow rate from these experiments and on earlier experiments conducted in 1975, the parameters in equation (3) have been determined as follows:

$$a = 0.045 \text{ and } b = 0.67$$

Given information on upstream and tributary inputs, the flow routing model simulates stream flow by solving equation (1) with K defined through equations (2) and (3).

The water quality models for the Bedford Ouse are similarly based on a mass balance principle but include factors to allow for the non-conservative nature of water quality variables. For example dissolved oxygen in the river is a balance between the various sources and sinks of oxygen. On the one hand there is oxygen supplied by the reaeration from the atmosphere and photosynthetic oxygen produced by plants and algae and, on the other hand, oxygen is being consumed by respiration processes and the removal of oxygen during the bacterial breakdown of organic material and effluents. The mass balance equations developed to simulate water quality behaviour are as follows:

Chloride

$$\frac{dx_1(t)}{dt} = \frac{Q_i(t)}{V} u_i^1(t) - \frac{Q_o(t)}{V} x_1(t) + S_1(t) \tag{4}$$

Nitrate

$$\frac{dx_2(t)}{dt} = \frac{Q_i(t)}{V} u_i^2(t) - \frac{Q_o(t)}{V} x_2(t) - k_1 x_2(t) + S_2(t) \tag{5}$$

Ammonia

$$\frac{dx_3(t)}{dt} = \frac{Q_i(t)}{V} u_i^3(t) - \frac{Q_o(t)}{V} x_3(t) - k_2 \left(\frac{1}{Q_o(t)}\right) x_3(t) + S_3(t) \tag{6}$$

Dissolved oxygen (DO)

$$\frac{dx_4(t)}{dt} = \frac{Q_i(t)}{V} u_i^4(t) - \frac{Q_o(t)}{V} x_4(t) - 4.33\, k_2 \left(\frac{1}{Q_o(t)}\right) x_3(t) - k_3 x_5(t)$$

$$+ k_4 (C_s(t) - x_4(t)) + S_4(t) \tag{7}$$

Biochemical Oxygen Demand (BOD)

$$\frac{dx_5(t)}{dt} = \frac{Q_i(t)}{V} u_i^5(t) - \frac{Q_o(t)}{V} x_5(t) - k_3 x_5(t) + S_5(t) \tag{8}$$

where x refers to the downstream (reach output) concentration mg/l;
u refers to the upstream (reach input) concentration mg/l;

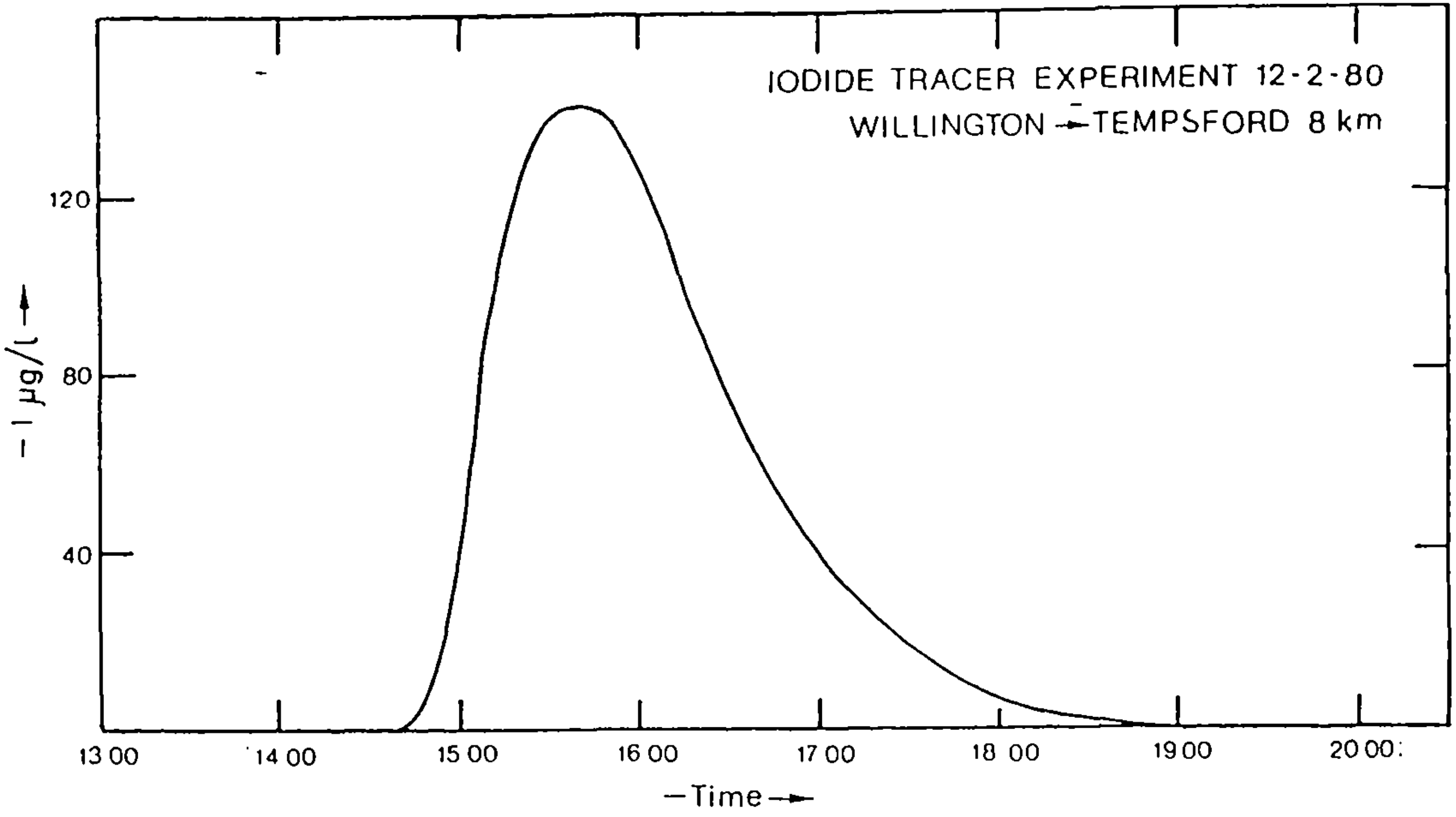

Figure 5 Tracer curve obtained from iodide tracer experiment conducted on 12.2.80 for Willington to Tempsford reach of the Bedford Ouse.

Q is the flow rate (determined from the flow model) and V is the reach volume;

S refers to the additional sources and sinks affecting water quality such as the net rate of addition of DO in the reach by photosynthetic/respiration activity of plants.

C_s is the saturation concentration of dissolved oxygen.

The model has been programmed to run in two modes.

(1) normal operating model, in which information on upstream input flows and quality are taken from the outstations and forecasts produced for all downstream reach boundaries up to 80 hours ahead. Because of the considerable travel time on the river, downstream forecasts are based on measured upstream flow and quality. It is necessary, however, to forecast upstream conditions to provide reasonable forecasts for the upper reaches. Techniques for this are given in Whitehead et al (1979).

(2) Impulse mode, in which the operator can supply information on an upstream impulse discharge of a conservative pollutant, ammonia or BOD. The resultant simulation uses the current flow and river quality data and simulates the slug of pollutant moving down the river system. Again forecasts up to eighty hours ahead are available at all of the twenty reach boundaries.

It is assumed that weather conditions remain stable during this forecast period. It would be possible however to link existing rainfall gauges into the telemetry scheme to forecast flow and quality.

Figure 6 and 7 show a typical simulation in impulse mode. The output data from the model can be plotted either as a profile down the river at a specific time or else as a function of time at any selected reach boundary. Thus if information on say the location of the minimum is required the river profile would be plotted. If, however, it is required to know the likely time of arrival of a slug of pollutant at a given point the time-concentration curves would be plotted.

CASE STUDIES

(a) Milton Keynes Effluent

The operational aspects of the model have already been tested in a real situation when Bedford Sewage Division reported a loss of oxidative treatment at the Cotton Valley Sewage Treatment works and effluent containing elevated levels of ammonia was discharged into the river at Newport Pagnell. In order to protect the water supply at Bedford (Clapham abstraction) information was required on the likely ammonia concentrations at Clapham and the time of arrival of the pollutant. Simulating ammonia using the model indicated an arrival time of four days with concentrations of ammonia of 1.2 mg/l at Clapham. The observed levels at Clapham were 1.12 mg/l and the arrival time was 4 days 2 hours. In this situation the model provided valuable information for the management at the Clapham water abstraction plant and gave them effectively a four day warning.

(b) Bedford Effluent

The second case study relates to the release of unsatisfactory effluent from Bedford sewage works which resulted in a significant pulse of ammonia being

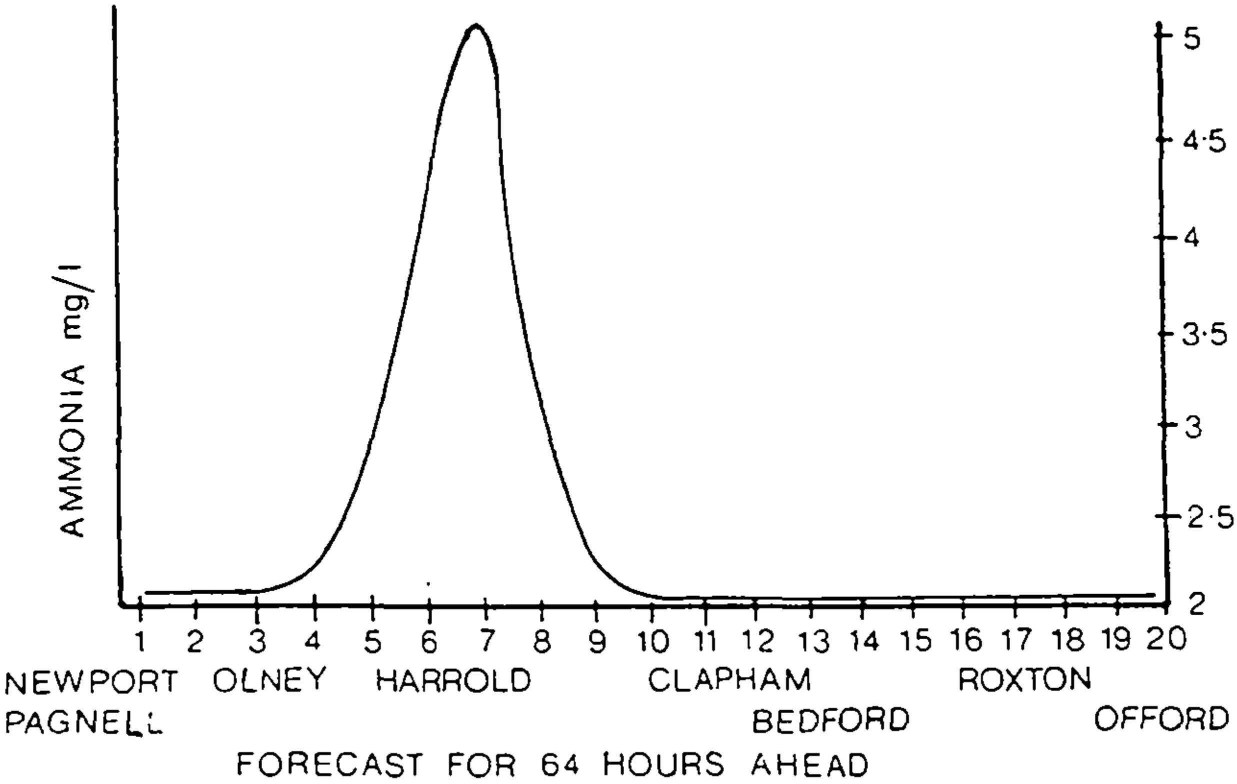

Figure 6 Ammonia Profile along Bedford Ouse

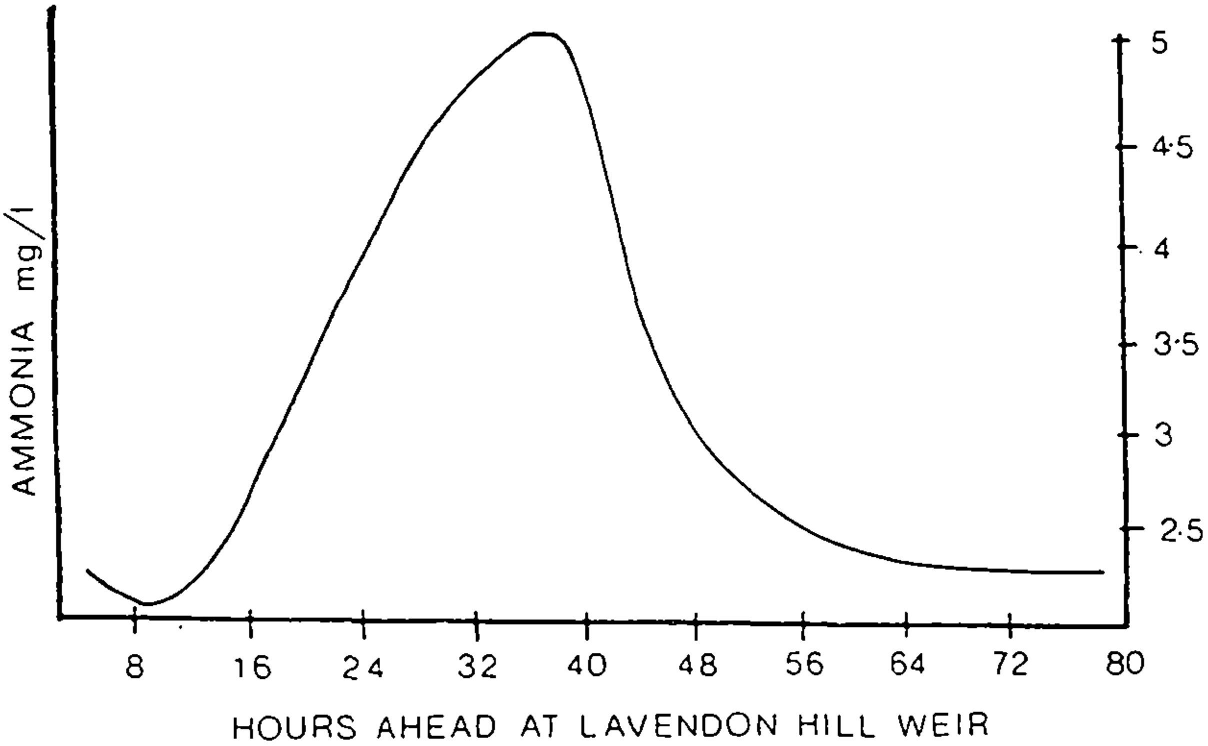

Figure 7. Ammonia forecast on Bedford Ouse

discharged to the river. Again—running the model in an impulse mode gave reasonable forecasts of ammonia and dissolved oxygen concentrations downstream at Tempsford (see Figure 8).

In both these situations information of value to pollution inspectors has been provided using the computer programs, monitoring and telemetry system. Such forecasts are of operational use and the flexible computing system installed on the Beford Ouse is essential if full use is to be made of the collected data.

FUTURE DEVELOPMENTS IN WATER QUALITY MONITORING

Considerable experience has been acquired over a number of years by the Great Ouse River Division of the Anglian Water Authority in the operation of automatic continuous water quality monitors. This experience has revealed the difficulties associated with operating existing monitors in the field, namely the fouling of electrode membranes with consequent signal drifting, difficulties in calibration and electrical interference. Since the AWA instrumentation is due for replacement over the next two years and additional stations are required, it was decided to initiate a study to develop a new intelligent micro-processor controlled pollution monitor.

The advantage of a micro-processor is that the distributed intelligence can be used locally to provide facilities such as data logging, automatic sensor calibration and cleaning local processing of data and control of pumps.

Description and Instrumentation

Figure 9 shows the front panel of the instrument. The water sample from the monitored stream is pumped to the equipment housed in a cubicle on the bank and in-line filtration is provided. On a timed basis, the complete sampling line is automatically cleaned by reversing the sample pump and blasting the intake line with compressed air to dislodge any undesirable accumulations of solids and growths. In a similar way automatic cleaning of the sensors is achieved.

The pre-amplifiers and sensors used are of proven quality and obtained directly from commercial sources. The variables to be monitored include pH, dissolved oxygen, temperature, electrical conductivity, ammonia, and nitrate. However, the general design accommodates other sensors and pre-amplifiers as they are developed.

In order to compensate for drift in performance sensors are periodically taken off-line, typically four times a day. After automatic cleaning they undergo standardisation against two levels of analytes of known concentration. Automatic resetting of the pre-amplifier output occurs to complete the automatic calibration cycle.

Facilities are included to record and report features of the monitor's status such as

(i) the rate of change of individual sensor output;
(ii) the stability of signals i.e. instrument noise;
(iii) temperature control;
(iv) reagent levels;
(v) performance of compressor and pumps;
(vi) leaks in pipe-work;
(vii) performance of control valving;
(viii) power supply status.

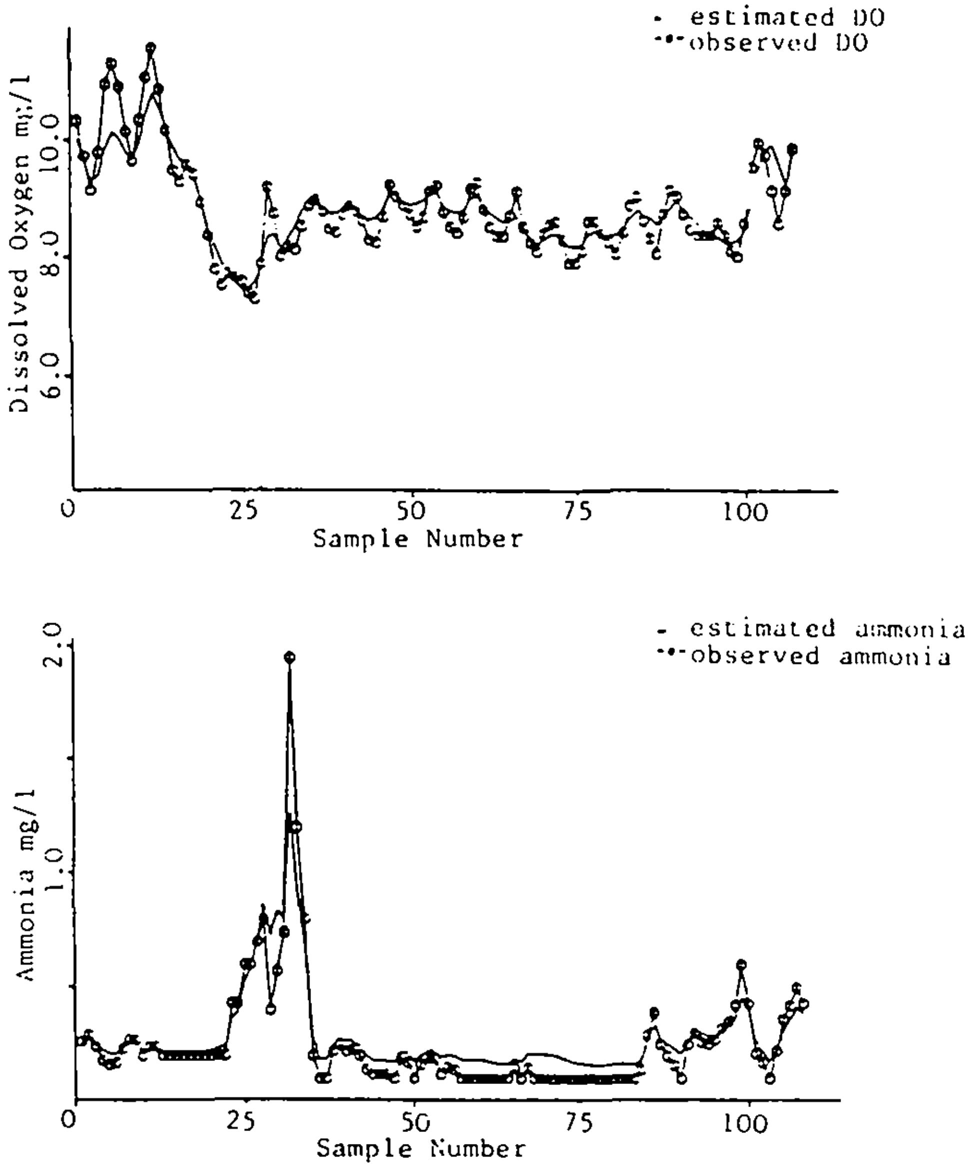

Figure 5 Dissolved Oxygen and Ammonia Forecast Downstream of Bedford

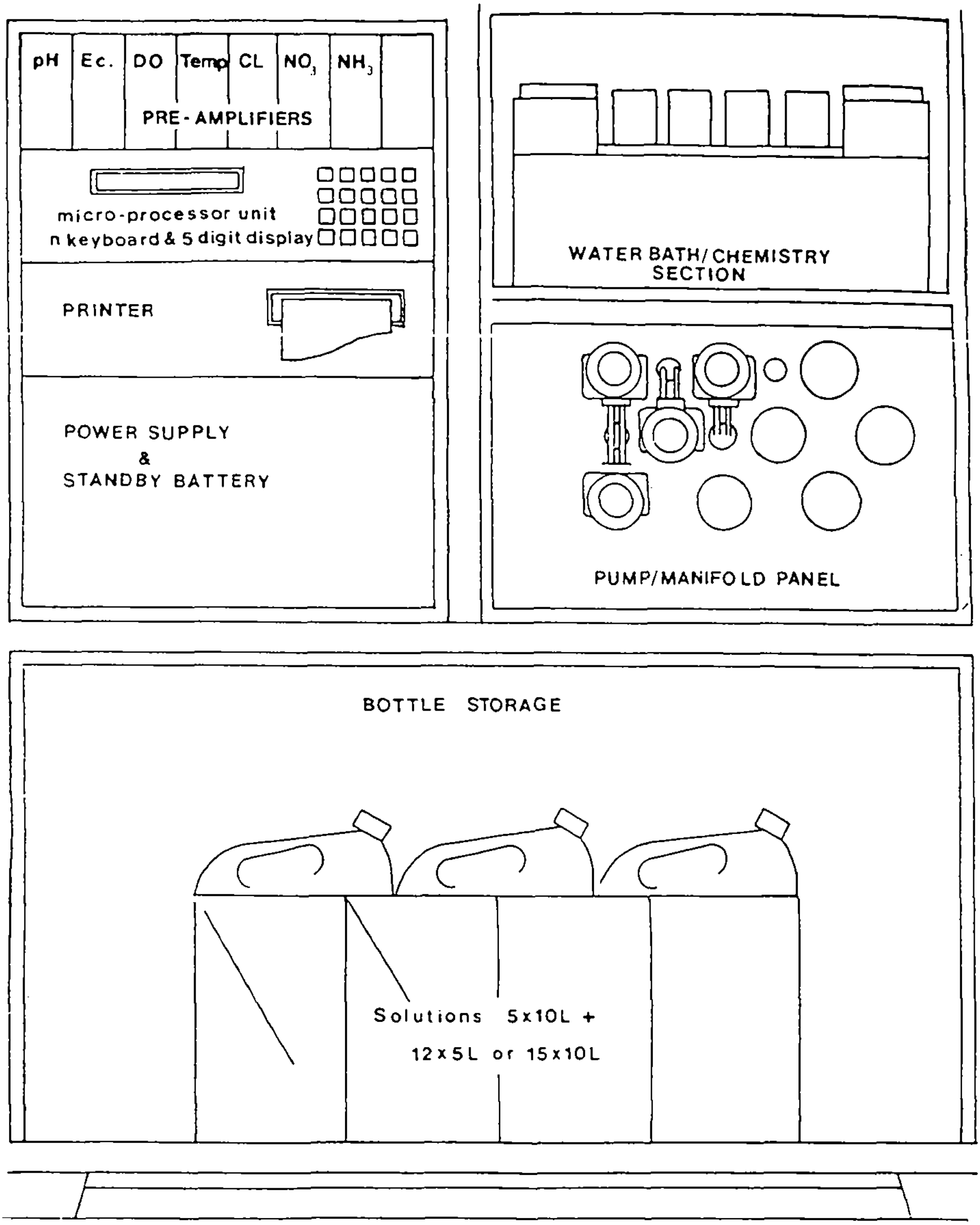

Figure Layout of Automatic Water Quality Monitor

Such status information is stored in the monitor's local memory for local output and telemetric relay to the central master station. When polluting conditions are detected the instrument is capable of checking the performance of its sensors in order to verify that the initially transmitted alarm is not really an instrument fault.

The design of the automatic chemistry unit housed in a constant temperature bath is already proven in respect of unit components. However, in assembling these components improvements over the performance, reliability and cost of existing instrumentation can be achieved. Examples of this integrity of design include the provision of "standby" heaters and pump motors capable of automatically taking over from "duty-units" should the latter prove faulty.

The positive features of the monitor's control depend on the advanced micro-electronic components and programming techniques used. Initially a rack of Euro-card standard electronic circuit boards is to be used. The cost of this section and of the pre-amplifiers would be further reduced eventually by re-configuring components on fewer and more compact boards.

All automatic processes such as the control of displays and telemetry and data handling are microprocessor driven. The process electronics are connected to a battery capable of supporting the logic for at least three days should mains power be lost. The programming is peformed using a threaded interpretive language, based on "Forth", a new programming technique which can allow a large reduction in development time compared with previous practice.

The memory is capable of storing data on hourly concentrations of pollutants and all status information. Output at the station or at the central station would be via robust alpha-numeric displays and via low cost matrix printers. Graphical and numerical output would be available suitably referenced to time, concentration units, site and variable name. Should the matrix printer fail, data would not be irrevocably lost, as in the case when more expensive continuous analogue recorders malfunction.

The direct control of outstation processes from a master station would be possible thereby making considerable savings in journey times and costs. Another novel feature would be the provision of a speech output at the central control station. The master station could be telephoned or could telephone given numbers in the event of pollutions. A true spoken message of the rivers status could be given in any required language.

The new instrument is currently undergoing development and should be available for detailed testing in 1983.

CONCLUSIONS

A mini-computer has been used to aid management in the operational control of water quality. The system developed for on line monitoring and forecasting has been generalised so that it is applicable to a wide range of telemetry schemes used within the water industry. The interactive programs allows for easy operational application and are designed for use by river management.

The data management system provides an efficient means of logging, converting and storing data. At the same time the models yield forecasts of flow and water quality at key locations along the river. Finally the new IH water quality monitor will enhance the reliability of water quality monitoring systems and together with the central mini-computer and telemetry control provide a cost effective tool for operational management.

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BEDFORD OUSE WATER QUALITY MODEL

USER MANUAL

CONTENTS

Introduction

This user manual sets out how to use the Bedford Ouse Water Quality Model and to display the results using the built in graphics package on the Minc-II.

The Bedford Ouse is modelled in five sections, each section is subdivided into a number of reaches. A list of reach boundaries is given in Appendix 1.

The model consists of a series of interactive forms and menus. At each stage of the model run, the user can edit or ammend data to his/her satisfaction before allowing the model to continue.

The following sections set out, in a logical order, how each of the forms and menus should be used. At the end of each section, an example is given to demonstrate the instructions given in the previous text.

Setting Up the data for a model run

The Bedford Ouse model is driven by a combination of menus and forms. This means that the user inputs the information by selecting options from a list.

2.1 Menus

A menu is a list of numbered options from which the user must select the number which represents the action required. The main menu is the one to which the model returns after completing each stage of a run. This allows the go through the required sequence of actions, ommitting any stages which are not necessary, to a complete a model run and to plot the data output from th run.

The user may select options in two ways

Using the Cursor

The cursor can be moved up and down the screen using the up/down arrow keys on the righthand side of the keyboard. When the cursor is level with the option required, the user must press the return key to select this option.

iii) Entering Numbers

If the user types in the number of the option required, the cursor will move to that number on the screen and the option will be executed by pressing the return key.

2.2 Forms

A form screen is used to define parameters. It consists of several questions with a space (data field) after it into which the value of the parameter is typed. If there are several possible answers, a list is usually given from which a value maybe chosen parameter. If no options are listed, the user may input any reasonable value.

There are several ways in which the user may input a value in the data field.

Using the PF2 and PF3 keys.

These can be used to increment and decrement any parameters which have a limited number of values. The PF2 key is used to increment a variable by one unit for each depression - the PF3 key decreases the value in the same way.

```
example   Sections to run? [     ALL] ALL, 123, 345, 1,2,3,4 OR 5.
```

If the PF2 key is pressed, the value will change from 'ALL' to '123'. If the PF3 key had been pressed, the value would have become '5'.

Thus, with these two keys, it is possible to step through each available option.

ii) Typing in the values or options

This may be done by typing a value in any part of the data field and pressing the return key. The new value then will overwrite anything currently allocated to the variable.

```
example   Entry Point? [              1.01] Brackley
```

If the users edits the data field.

```
          Entry Point? [5             1.01] Brackley
```

When this value is entered it will show:

```
          Entry Point? [              5.01] Roxton.
```

If the user wishes to input a word, it is not usually necessary to type the whole word because the model recognises the first letter and will automatically assume the remainder of the word eg. if the letter 'F' is typed in, the model will recognise that to be 'Flow'. In this instance it would also be possible to type 'FL' or 'FLO'.

In order to move to the next line of the form, the user may press either the RETURN key, the TAB key or the up and down arrows which move the cursor. The cursor can be used to access any line on the form by using the arrow keys as necessary.

Once the user has edited a form screen to his satisfaction, he may proceed to the next stage of the model by pressing the PF1 key - the model will either return to the main menu, produce the next form, or plot the final graph.

If the user wishes to abandon a form at any stage he can press PF4 key which will return the model to the main menu without processing the information on the form.

2.3 Error Messages

The Bedford Ouse model incorporates a comprehensive set of error messages. Thus, if invalid information is input to the model, it is detected and an error message appears immediately the user attempts to enter it into the model run.

The error messages appear at the bottom of the screen, accompanied by a bleep, they explain the nature of the mistake and prevent the user from continuing until a valid value is input. The mistake is corrected by simply typing a new value over the incorrect one.

Control Functions

There are several control functions available on the Bedford Ouse model. They are used by pressing the control key at the some time as pressing another - key usually a letter. eg 'control + W' means press the control key (the key marked 'CNTL' on the left hand side of the keyboard) and the 'W' key simultaneously.

The following functions are available:

Control + W - rewrites the screen if it becomes corrupted. ie if characters appear on the screen when they should not.

ii) Control + E - erases the character that the cursor is currently centred upon.

iii) Control + R - shifts the curser one place to the right, inserting a blank space.

Control + T - erases the current data held from the current position the curser to the end of the field.

vi) Control + Z displays a selection without enetering it into the model. It will invoke error messages which would appear if incorrect data was entered.

vii) Control + ' this accesses the HELP system which is available during plotting routines. It lists options for certain parameters and it shows which reaches and profiles are available to be ploted. Once in HELP, the user is given precise instructions on its usage.

The user can erase characters using the delete key (this is the key marked 'DEL') this function deletes the character immediately before the cursor. If the key is kept drepessed, it will continue deleting along the line.

Running the Bedford Ouse Model

To begin the Bedford Ouse Model, the MINC-11 should be switched on at the terminal and at the disc drive.

When the disc has been switched on, the following will appear on your screen:

```
     RT-11FB (S) V05.01B

     .IND INITFB

Your console is a VT102

     Date [dd-mm-yy]?
```

Here the user should input data in the format:

```
     07-FEB-86
```

The screen will then show a time prompt:

Time [hh:mm:ss]?The user should input the time in the format:

```
     14:22:30
```

The screen will then display:

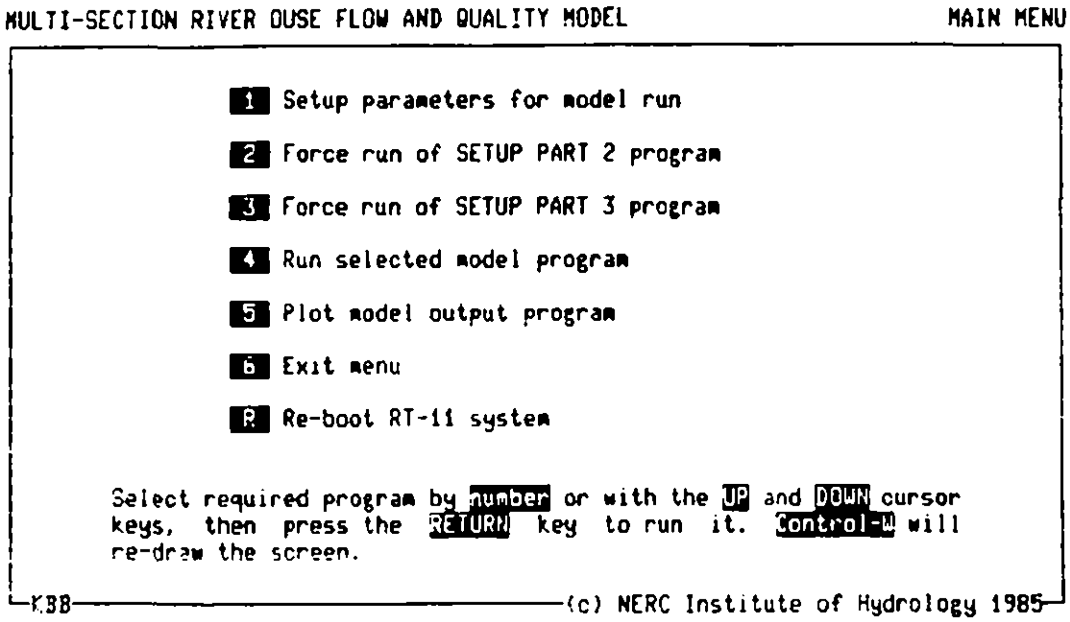
```
     14:22:34 Fri 07-Feb-1986

     Mount WQMW data disc indrive 1 and press RETURN -
```

This completes the initialization of the model, the run will then begin and the main menu will appear on the screen

Main Menu

The main menu is the point to which model returns after completing each stage of a run. From the menu, the user can control the run and access the data being used to edit it if required.



```
MULTI-SECTION RIVER OUSE FLOW AND QUALITY MODEL                 MAIN MENU

              1 Setup parameters for model run

              2 Force run of SETUP PART 2 program

              3 Force run of SETUP PART 3 program

              4 Run selected model program

              5 Plot model output program

              6 Exit menu

              R Re-boot RT-11 system

     Select required program by number or with the UP and DOWN cursor
     keys, then press the RETURN key to run it. Control-W will
     re-draw the screen.
KBB                              (c) NERC Institute of Hydrology 1985
```

Generally a complete model run consists of three stages:

Setting up the parameters (Option 1).

ii) Running the model (Option 4).

iii) Plotting the results (Option 5).

Each of these stages must be initiated by the user.

The options available allow the user to enter any stage of the model, thus he/she may skip certain procedures which are not needed for a run.

The details of each option are explained in this section.

4.2 Setup Parmeters for Model Run (Option 1)

This option consists of three setup forms for the user to complete:

Setup Part 1 this form allows the user to select the model run he wishes to perform. Once the parameters have been defined, the user may proceed to be next form by pressing the PF1 key.

) Setup Part 2 - this form allows the user to control the usage of the data files depending on the nature of the data available. Once this has been completed, the PF1 key will access the next form.

iii) Setup Part 3 - this is the final stage of the setup procedure, and allows the user to edit any data he wishes to change. Once this is completed, the main menu is returned to the screen.

4.2.1 Setup Part 1

) Sections to run?

The user is required to define which section of the river he/she wishes to model. This is done by selecting one option from the list given. The options cover all the combinations of river sections which can reasonably be modelled.

ii) Type of run?

The user may choose either the flow model or the impulse model:

a) Flow - This option predicts the flow and quality along the selected river section based on the most recently available data. If this option is chosen, the user may ignore the remaining parameters on the screen and proceed to Setup Part 2.

b) Impulse (option A, B, or C) - this models the effect of the input of a pollutant to the river at a particular point, over a specified length of time. The option selected by the user specifies the nature of the pollutant:

- ammonia

B - biological oxygen demand

- conservative

iii) Duration

Redundant for flow models.

This parameter allows the user to specify the duration* of the pollutant input ie. the length of time over which it was discharged into the river.

The time is input in units of 8 hours eg. 2 = 16 hours.

iv) Concentration?

Redundant for flow models.

The user must input the concentration (mg/ℓ) of the pollutant being discharged into the river.

v) Flow Rate?

Redundant for flow models.

The user inputs the rate (cumecs or m^3/ sec) at which the pollutant is being discharged into the river.

vi) Entry Point

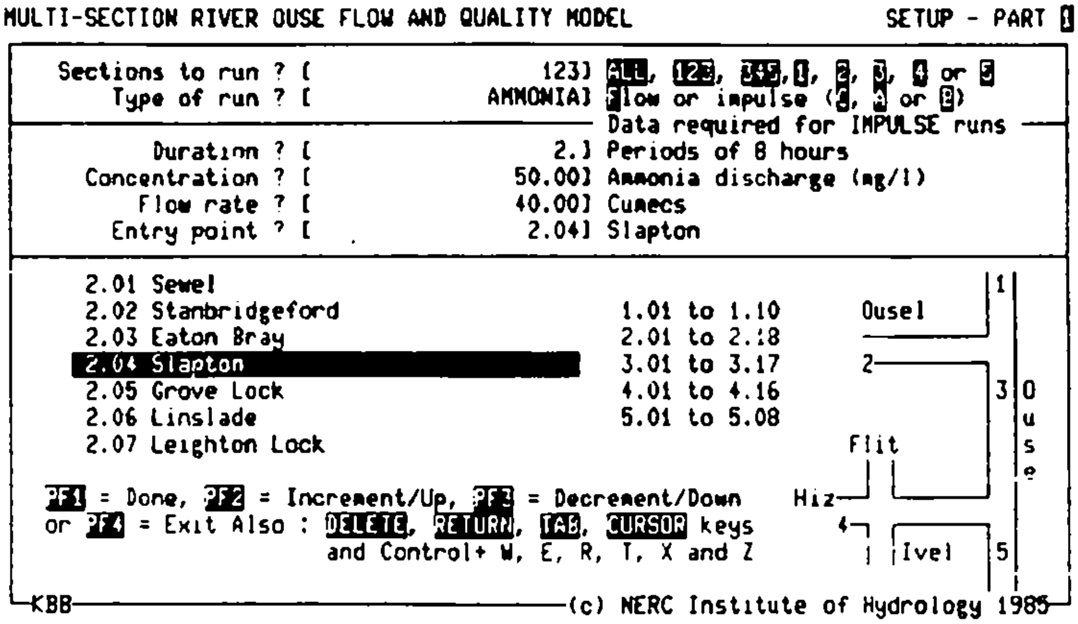
Redundant for flow models.

This allows the user to specify the point at which the pollutant is discharged into the river. The location is referred to using the number of the nearest named reach, these are listed in Appendix 1.

Example.

This form has been set up to run the model on sections 1, 2 and 3 of the river. The model will develop an impulse model for an ammonia discharge at Slapton which last 16 hours with a flow rate of 40 m^3/s with a concentration of 50 mg/ℓ.

A diagram of the River Ouse, with the section numbers labelled, is shown on the bottom half of the screen. There is also a list of the reaches immediately upstream and downstream of the impulse. The reach which has been named as the entry point for an impulse is written in black with a white background.



```
MULTI-SECTION RIVER OUSE FLOW AND QUALITY MODEL                    SETUP - PART 1

    Sections to run ? [                   123] ALL, 123, 345, 1, 2, 3, 4 or 5
        Type of run ? [              AMMONIA] Flow or impulse (F, A or B)
                                              Data required for IMPULSE runs
           Duration ? [                    2.] Periods of 8 hours
      Concentration ? [                50.00] Ammonia discharge (mg/l)
          Flow rate ? [                40.00] Cumecs
        Entry point ? [                 2.04] Slapton

      2.01 Sewel                                                          1
      2.02 Stanbridgeford                   1.01 to 1.10       Ousel
      2.03 Eaton Bray                       2.01 to 2.18
      2.04 Slapton                          3.01 to 3.17       2
      2.05 Grove Lock                       4.01 to 4.16                  3 O
      2.06 Linslade                         5.01 to 5.08                    u
      2.07 Leighton Lock                                      Flit          s
                                                                            e
  PF1 = Done, PF2 = Increment/Up, PF3 = Decrement/Down      Hiz
  or PF4 = Exit Also : DELETE, RETURN, TAB, CURSOR keys      4
                         and Control+ W, E, R, T, X and Z        Ivel     5
KBB------------------------------------(c) NERC Institute of Hydrology 1985
```

4.2.2 Setup Part 2

Maximum Time Difference?

In order to obtain sensible results, the model must be run with a coherent data set. This means that data from the outstations used to run the model for a particular section must have been measured at approximately the same time.

Example.

To run the model for section 5, data from sections 3 and 4 are combined. The results will therefore be meaningless unless both sets of data were measured at the same time.

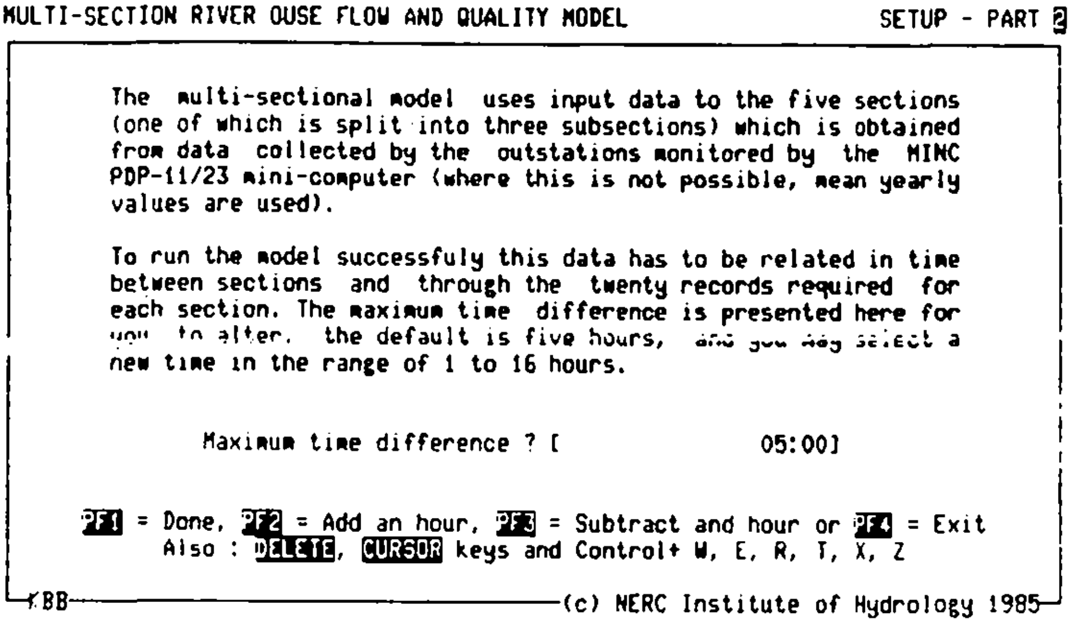
If the data available for the sections is not sufficiently close in time, the previous times will be scanned until the most recent sets of data which are close enough in time are found.

The Maximum Time Difference option allows the user to specify the maximum difference between the data sets which can be tolerated. The model will accept any value up to 16 hours.

If no valid data is available, within the time limit specified, the model will substitute the average annual values.

Example

This form is set up for a maximum time difference of 5 hours. This means that if data for a certain variable is not availale for a given time, the nearest valid value within ± 5 hours of the time will be substituted.



```
MULTI-SECTION RIVER OUSE FLOW AND QUALITY MODEL                 SETUP - PART 2

         The  multi-sectional model  uses input data to the five sections
         (one of which is split into three subsections) which is obtained
         from data  collected by the  outstations monitored by  the  MINC
         PDP-11/23 mini-computer (where this is not possible, mean yearly
         values are used).

         To run the model successfuly this data has to be related in time
         between sections  and  through the  twenty records required  for
         each section. The maximum time  difference is presented here for
         you  to alter.  the default is five hours,  and you may select a
         new time in the range of 1 to 16 hours.


                Maximum time difference ? [                 05:00]


      PF1 = Done, PF2 = Add an hour, PF3 = Subtract and hour or PF4 = Exit
           Also : DELETE, CURSOR keys and Control+ W, E, R, T, X, Z

 KBB----------------------------------------(c) NERC Institute of Hydrology 1985
```

4.2.3 Setup Part 3

i) Section being edited?

The user must specify which section of the river he wishes to alter. It is not possible to edit sections which are not being used for the model run.

ii) For each section of the river being modelled, ten records are used to supply data for each reach of river over a period of time. The user may choose to change any parameters in any of the records for the section being edited.

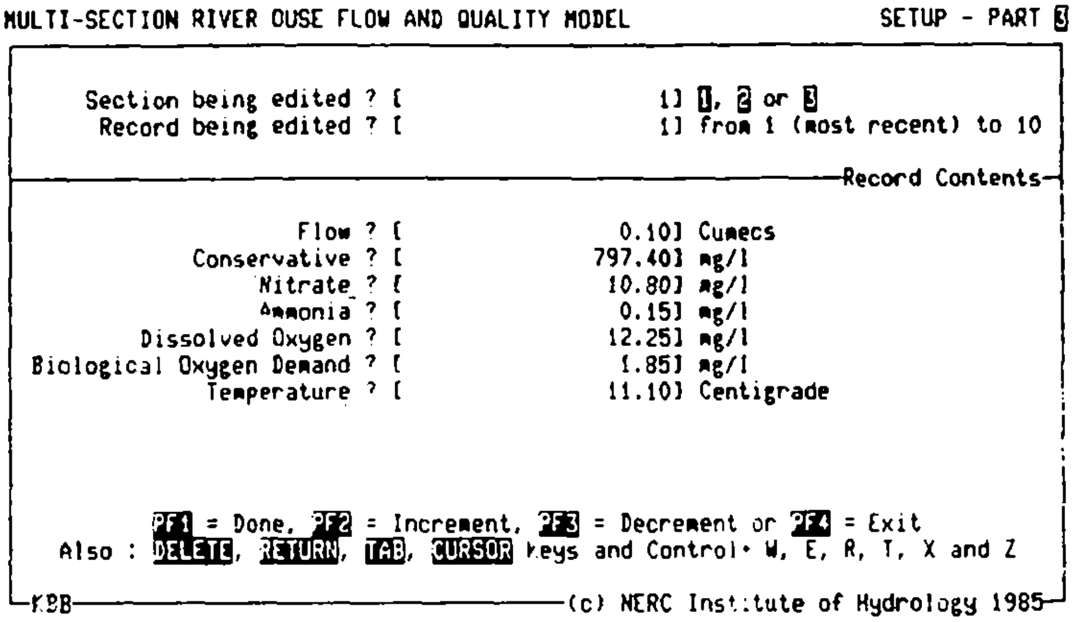
The records for each reach are numbered fro 1 to 10, the tenth record being the most recent data available.

The variables in a record which is to be edited are listed on the screen with their existing values displayed. The variables given are:

Flow (cumecs)
Conservative (mg/ℓ)
Nitrate (mg/ℓ)
Ammonia (mg/ℓ)
Dissolved Oxygen (mg/ℓ)
Biological Oxygen Demand (mg/ℓ)
Temperature (Centigrade)

Example

This form is set up to edit the most recent record for section 1 of the river. The values for this record are listed in the bottom section of the screen as they will be used in the model.



```
MULTI-SECTION RIVER OUSE FLOW AND QUALITY MODEL                SETUP - PART 3
┌─────────────────────────────────────────────────────────────────────────────┐
│     Section being edited ? [                 1] 1, 2 or 3                    │
│      Record being edited ? [                 1] from 1 (most recent) to 10   │
├──────────────────────────────────────────────────────────Record Contents────┤
│                       Flow ? [            0.10] Cumecs                       │
│               Conservative ? [          797.40] mg/l                         │
│                    Nitrate ? [           10.80] mg/l                         │
│                    Ammonia ? [            0.15] mg/l                         │
│           Dissolved Oxygen ? [           12.25] mg/l                         │
│  Biological Oxygen Demand ? [             1.85] mg/l                         │
│                Temperature ? [           11.10] Centigrade                   │
│                                                                             │
│                                                                             │
│           PF1 = Done, PF2 = Increment, PF3 = Decrement or PF4 = Exit        │
│   Also : DELETE, RETURN, TAB, CURSOR keys and Control- W, E, R, T, X and Z  │
└KPB─────────────────────────────────────(c) NERC Institute of Hydrology 1985─┘
```

4.3 Force run of SETUP PART 2 program (Option 2)

The user may wish to run the model several times using different parameters for each run. To do this it is possible to enter the setup routine at different points to give access to certain variables without having to start at the beginning.

This option allows the user to enter the program at Setup Part 2 (see Section 4.2.2). The model then continues onto Setup Part 3.

4.4 Force run of SETUP PART 3 program (Option 3)

This is the same facility as Section 4.3, except it allows the user to enter the model at Part 3 (see Section 4.2.3).

4.5 Run Selected Model (Option 4)

This section of the model is not interactive. Once the option has been selected, the 'Please Wait' prompt is displayed and the number of the reach being processed is shown in the top left hand corner of the screen.

When the model has completed its run, the screen returns to the main menu.

4.6 Plot Model Output Program (Option 5)

i) Data Source?

This option allows the user to specify the type of plot he/she wishes to produce. It is possible to plot either flow or impulse models separately, or both together on the same graph.

If the user attempts to plot a model which has not been run for the current data set, the resulting graph will use the previous data set.

ii) Determinand?

This allows the user to specify which variable he/she wishes to plot. There are several options available:

Flow
Conservative
Ammonia
Nitrate
Dissolved Oxygen
Biological Oxygen Demand

The options may be stepped through using the PF2 and PF3 keys, or may be selected by typing the first letter of the variable name.

iii) Plot Type?

This may be one of two options:

Profile - a plot of the variation in water quality characteristics at a selected instant in time, over a specified length of river.

b) Reach - a plot of the variation in water quality characteristics at a selected section of river, over a specified time interval.

iv) First reach for profile?

Redundant for reach plots

This allows the user to specify the number of the point at which the profile plot is to begin.

v) Last reach for profile?

Redundant for reach plots.

This allows the user to specify the number of the point at which the profile plot is to end.

vi) Time profile?

Redundant for reach plots.

In an impulse model, the time is taken to be the number of hours after the input of the pollutant. In a flow model, this is the number of hours ahead from the present time (ie from the most recent data available).

This allows the user to specify the time at which the profile is to be plotted.

The time is given in units of 8 hour periods eg. 2 = 16 hrs.

vii) Reach for reach plots?

Redundant for profile plots.

This allows the user to specify the point at which the reach model to be plotted by inputting the number of the nearest named point on the river.

viii) First time for reach plot?

Redundant for profile plots.

This is the time as specified in 4.6 (vi).

Here the user may specify the time at which the model should begin, again, in units of 8 hour periods.

The time may be anything between 8 and 80 hours (ie 1-10 units).

ix) Last time for reach plot?

Redundant for profile plots.

Here the user may specify the time at which the reach plot should end, as above:

x) Auto scale Y axis?

If the YES option is selected, the horizontal axis for the graph is automatically scaled between the maximum and minimum values of the determinand.

If the NO option is selected, the user must then specify the values he wishes to be used for the plotting (see below).

xi) Y axis minimum?

Redundant if auto scale Y axis is YES

This allows the user to select the m[illegible]e for the Y axis

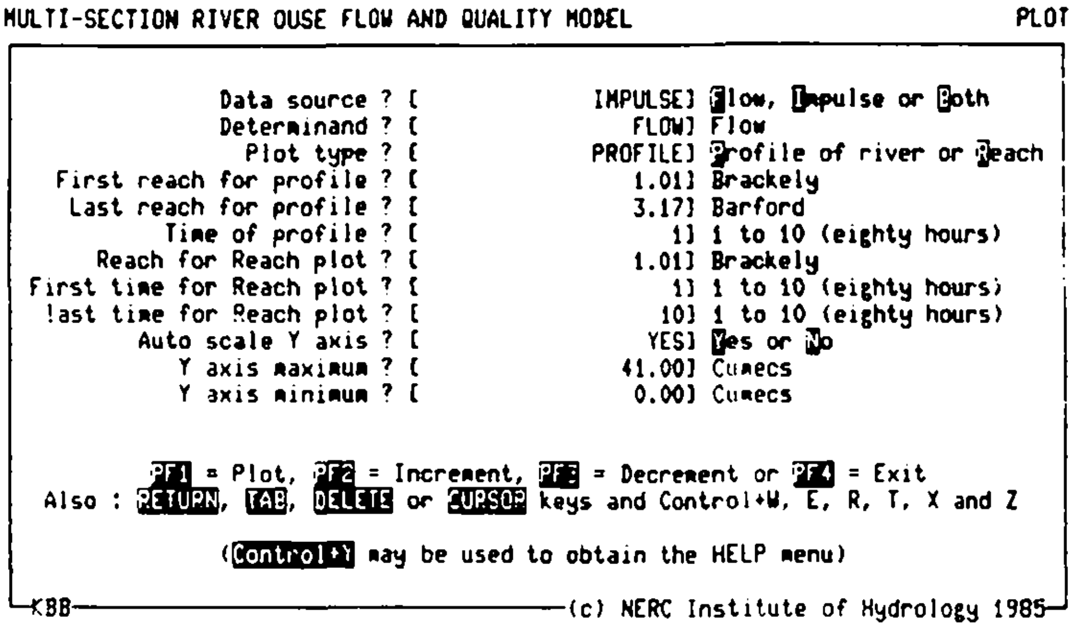
xii) Y axis maximum?

Redundant of auto scale Y axis is YES

This allows the user to specify the [illegible]lue for the Y axis.

Example

The output produced from this form will be a graph showing the river flow resulting from an impulse of ammonia (see the example for Section 4.2.1). The plot will be a profile between Brackley and Barford taken 8 hours after the impulse. The y axis will automatically be scaled between the maximum and minimum values of the flow.



```
MULTI-SECTION RIVER OUSE FLOW AND QUALITY MODEL                              PLOT

                 Data source ? [                 IMPULSE] Flow, Impulse or Both
                 Determinand ? [                    FLOW] Flow
                   Plot type ? [                 PROFILE] Profile of river or Reach
     First reach for profile ? [                    1.01] Brackely
      Last reach for profile ? [                    3.17] Barford
             Time of profile ? [                       1] 1 to 10 (eighty hours)
        Reach for Reach plot ? [                    1.01] Brackely
   First time for Reach plot ? [                       1] 1 to 10 (eighty hours)
    Last time for Reach plot ? [                      10] 1 to 10 (eighty hours)
           Auto scale Y axis ? [                     YES] Yes or No
              Y axis maximum ? [                   41.00] Cumecs
              Y axis minimum ? [                    0.00] Cumecs


          PF1 = Plot, PF2 = Increment, PF3 = Decrement or PF4 = Exit
  Also : RETURN, TAB, DELETE or CURSOR keys and Control+W, E, R, T, X and Z

               (Control+Y may be used to obtain the HELP menu)
KBB                                      (c) NERC Institute of Hydrology 1985
```

4.7 Exit Menu (Option 6)

This gives access to the operating system for the Minc II. Usually this option is reserved for debugging purposes only. If this option is selected, the prompt will be a '. ' and the user may return to the main menu by typing 'R MENU' .

4.8 Re-boot the RT-11 system (Option R)

This allows the system to be completely re-initialised. Again, this will not normally be needed for normal use of the model. When this option is selected, the system will return to the stage described in Section 4, except the date and time will not be requested again.

APPENDIX I

Reach Number	length of Reach (m)	Name of Reach	Name of River
1.01	3750.	Brackely	OUSE
1.02	7250.	Westbury	OUSE
1.03	3000.	Tingewick Mill	OUSE
1.04	4000.	Bourton Bridge	OUSE
1.05	4500.	Thorborough Mill	OUSE
1.06	4500.	Beachampton	OUSE
1.07	4250.	Stoney Stratford Weir	OUSE
1.08	2250.	Cosgrove Lodge Park	OUSE
1.09	7000.	New Bracknell	OUSE
1.10	2750.	Quarry Hall	OUSE
2.01	2000.	Sewel	OUSEL
2.02	2300.	Stanbridgeford	OUSEL
2.03	2250.	Eaton Bray	OUSEL
2.04	2400.	Slapton	OUSEL
2.05	1800.	Grove Lock	OUSEL
2.06	2300.	Linslade	OUSEL
2.07	3000.	Leighton Lock	OUSEL
2.08	2500.	Heath Mill	OUSEL
2.09	2000.	Stapleford Mill	OUSEL
2.10	2250.	Paper Mill Farm	OUSEL
2.11	1500.	Westfield Farm Mill	OUSEL
2.12	2300.	Waterhall	OUSEL
2.13	2500.	Fenny Stratford	OUSEL
2.14	2250.	Wlaton	OUSEL
2.15	2500.	Waughton on the Green	OUSEL
2.16	1900.	Milton Keynes Village	OUSEL
2.17	2300.	Willen Weir	OUSEL
2.18	2300.	Wepemer	OUSEL
3.01	5200.	Newport Pagnell	OUSE
3.02	3000.	Tyringham Bridge	OUSE
3.03	4300	Revenstone Weir	OUSE
3.04	4000.	Olney Weir	OUSE
3.05	4500.	Lavendon Mill Weir	OUSE
3.06	5300.	Turvey	OUSE
3.07	3040.	Harrold Weir	OUSE
3.08	2850.	Felmersham	OUSE
3.09	6260.	Stafford Bridge	OUSE
3.10	3370.	Oakley Weir	OUSE
3.11	2220.	Clapham	OUSE
3.12	4000.	Bromham Weir	OUSE
3.13	5150.	Bell End	OUSE
3.14	2080.	Cardington	OUSE
3.15	1880.	Castle Mill	OUSE
3.16	2240.	Willington	OUSE
3.17	4320.	Barford	OUSE
4.01	4500.	Ickleford	HIZ
4.02	3500.	Arlesey	HIZ
4.03	2750.	Flitwich	FLIT
4.04	3250.	Claphill	FLIT
4.05	2300.	Beadlow	FLIT
4.06	2000.	Chicksands	FLIT
4.07	2400.	Shefford	FLIT
4.08	2750.	Clifton Manor	FLIT
4.09	1300.	Radwell	IVEL
4.10	3000.	Stotford	IVEL
4.11	3300.	Astwick	IVEL
4.12	5000.	Henlow	IVEL
4.13	4500.	Langford Mill	IVEL
4.14	3750.	Biggleswade	IVEL
4.15	4000.	Beeston	IVEL
4.16	2750.	Blunham Weir	IVEL
5.01	7500.	Roxton	OUSE
5.02	4000.	Eaton Socon	OUSE
5.03	7250.	St. Neots	OUSE
5.04	4000.	Offord	OUSE
5.05	7750.	Brampton	OUSE
5.06	6500.	Wyton	OUSE
5.07	4000.	St. Ives	OUSE
5.08	4500.	Holywell	OUSE

SECTION 3 - MODELLING HEAVY METALS IN RIVER BASINS - THE RIVER TAWE STUDY

MODELLING HEAVY METALS IN RIVER BASINS

3.1 Introduction

The heavy metals study has been undertaken to investigate the movement, distribution and modelling of heavy metals in river systems. A considerable data base has been established for the River Tawe in South Wales and important background information and data analysis is presented elsewhere (Whitehead et al 1984)

Figure 3.1 shows the section of the River Tawe modelled, the main tributaries and the two Welsh Water Authority gauging stations. For modelling purposes the section has been divided into four reaches which were chosen to coincide with the sampling sites of the Welsh Water Authority and the 5-week survey described elsewhere These sampling sites themselves were chosen to isolate the major effluents that enter the River Tawe. The reach structure together with the main effluents and tributaries is shown schematically in figure 3.2.

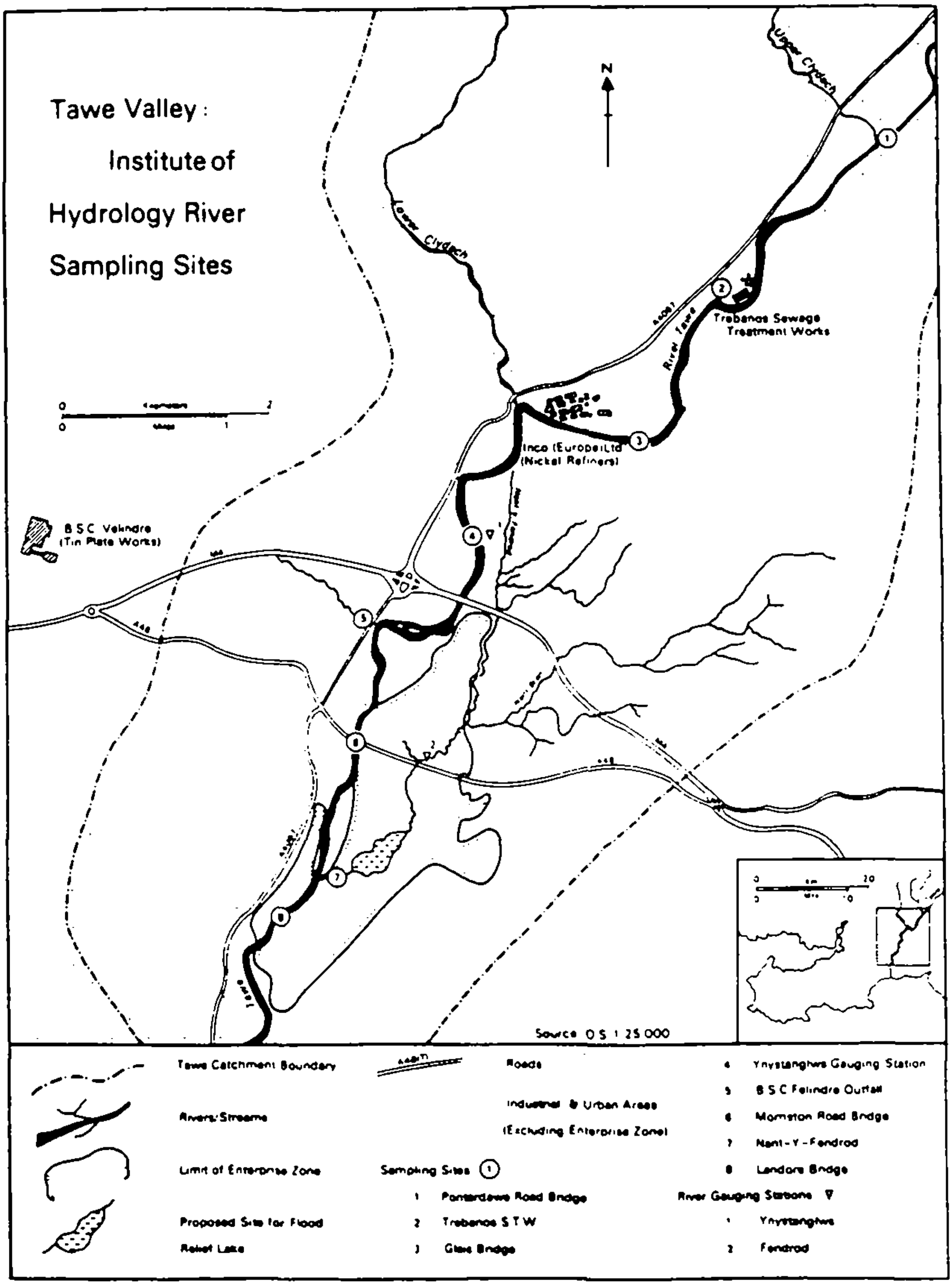
3.2 The catchment flow model

3.2.1 Main Channel model

A detailed description of the flow model is provided in Whitehead et al, 1979, a summary is included here. The model is based on a multiple reach representation of a river in which each reach is characterised by a number of compartments. The model for flow variations in each compartment is based on an analogy with the lumped parameter e quations for the variations in concentration of a conservative pollutant under the assumption of uniform mixing over the compartment (Whitehead et al, 1979). Alternatively, the model may be viewed in hydrological flow routing terms as one in which the relationship between inflow I, outflow Q and storage S in each compartment is represented by the differential equation

$$\frac{dS}{dt} = I - Q \qquad (3.1)$$

Figure 3.1 Map showing the modelled section of the River Tawe



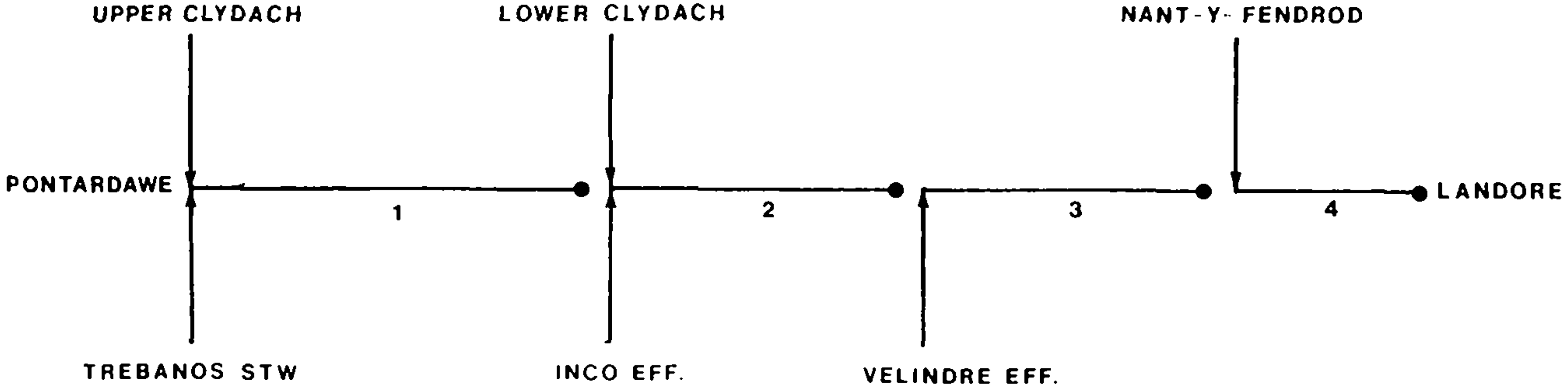


Figure 3.2 Reach structure for the River Tawe

with

$$S = KQ$$

where K is a travel time or residence time parameter. If K is fixed, then this does not allow any variation in travel time with flow; to achieve this, K is expressed as

$$K(Q) = \frac{L}{UN} \tag{3.2}$$

where N is the number of compartments in the reach, L is the reach length, and U, the mean flow velocity in the reach, is related to discharge through

$$U = aQ^{b} \tag{3.3}$$

where a and b are coefficients to be estimated. The resulting differential equation to be solved is then

$$\frac{dQ}{dt} \qquad \frac{a\ N}{L(1-b)} \quad Q^{b}\ (I-Q) \tag{3.4}$$

The value of N affects the relative importance of floodwave advection and dispersion in a reach; values of N, a and b can be determined by calibration using an observed record of downstream flow.

In the case of the River Tawe a large number of simultaneous velocity and flow measurements existed covering the period 1979-1982, for each of the reaches of interest. A simple regression of the logarithm of velocity against the logarithm of flow gave a very good fit for all reaches from which the a and b parameters defined in equation 3.3 could be calculated. The values for the a and b parameters plus the corresponding correlation coeficients are given in table 3.1.

Table 3.1 Velocity-Flow parameters for the River Tawe

Location	a parameter	b parameter	correlation coefficient
Pontardawe	0.19	0.64	0.97
Glais	0.12	0.64	0.75
Ynystanglws	0.05	0.64	0.90
Morriston	0.05	0.64	0.90

Given information on upstream and tributary inputs, the flow routing model can be used to derive simulations of downstream flow by solving equation (3.4) using a numerical integration routine with a variable step length. This is particularly useful since under periods of low flow and high residence times, the integration step length can be increased, thereby saving computer time. Under high flow conditions, however, residence times are reduced and in order to solve the equation to the same accuracy, it is necessary to reduce the integration step length. Since this is achieved automatically, there are relatively few numerical integration problems.

3.2.2 Estimating tributary and effluent inputs

There are three main tributaries entering the River Tawe in the modelled section. The Upper Clydach enters just below Pontardawe, the Lower Clydach enters midway between Glais and Ynystanglws and the Nant-y-Fendrod which joins the Tawe just upstream of Landore. The Nant-y-Fendrod is the only one of these which is continuously gauged. The other two have had spot gaugings carried out over a number of years and sufficient values existed to regress the values with those taken at the main gauging station on the River Tawe at Ynystanglws.

This produced an equation that could be used to calculate flow rates for the Upper and Lower Clydach from the continuously recorded flow at Ynystanglws of the form

$$T_i = a_i Q + b_i \tag{3.5}$$

where T_i is the tributary flow to be estimated (cumecs), Q is the recorded flow at Ynystanglws (cumecs) and a_i and b_i are the regressions parameters of the i^{th} tributary. The values of a_i and b_i are given in Table 3.3 with the corresponding correlation coefficient.

Table 3.3 Regression parameters for tributary estimation equations

Tributary	**a parameter**	**b parameter**	**correlation coefficent**
Upper Clydach	0.078	0.03	0.91
Lower Clydach	0.062	0.25	0.82
Tawe at Pontardawe	0.713	0.02	0.96

The Tawe at the top of the modelled section, Pontardawe, is also ungauged and a similar exercise to that undertaken for the Upper and Lower Clydach was carried out to estimate flows at this point, again a good fit was obtained, Table 3.3.

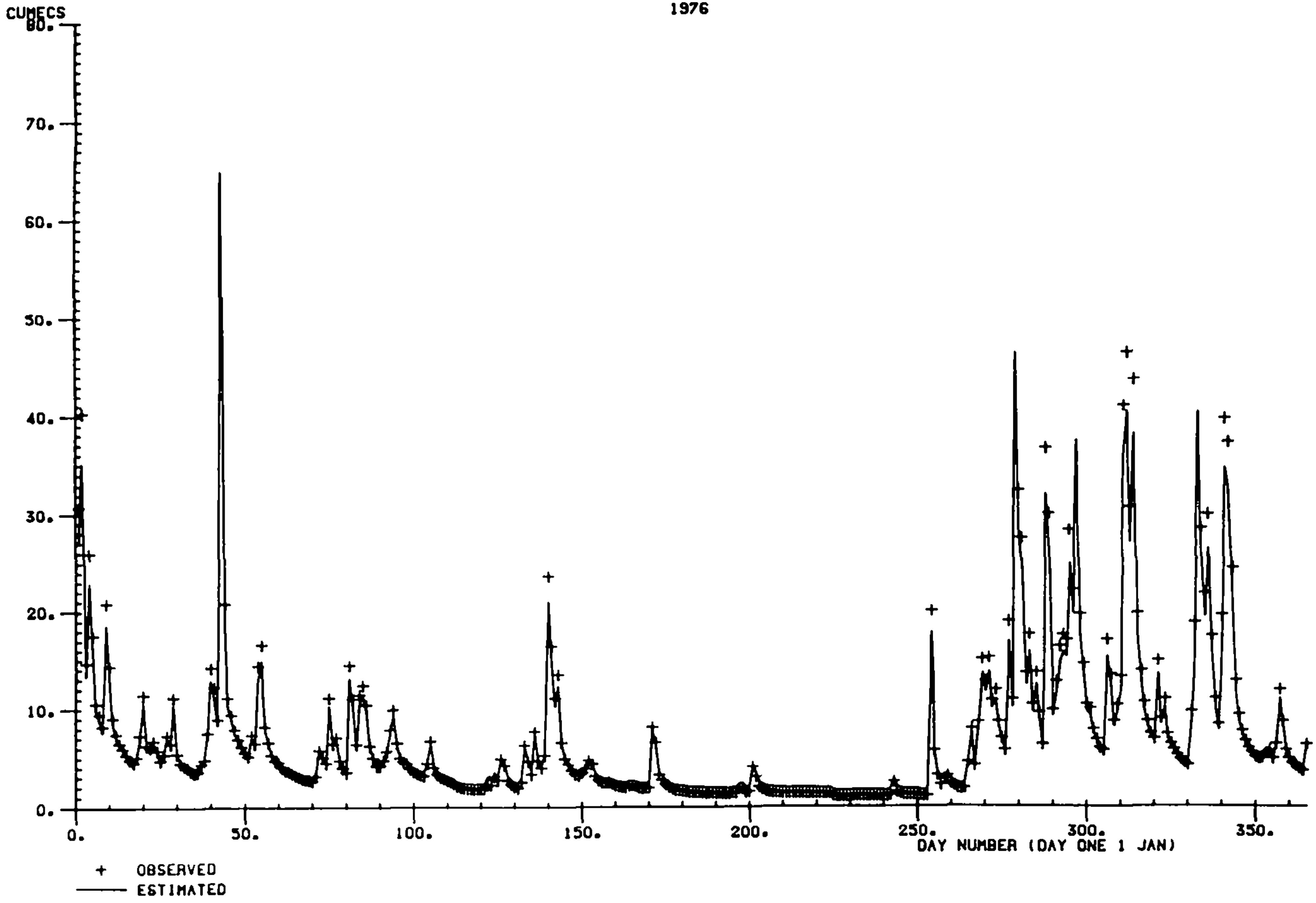
The quantity of effluent that may be discharged to the Tawe by any industrial plant is subject to limits imposed by the Welsh Water Authority. For the purposes of modelling it was assumed that both the British Steel Works at Velindre and the INCO works at Clydach discharged at their maximum allowed rate at all times. This is probably not the case since the discharge rate will go up and down with production but this variation should not be significant when compared with the variation in river flowrate

The sewage treatment works at Trebanos is gauged but in practice the through-put rarely dropped below the maximum and hence was considered to be constant in the model.

3.2.3 Combined tributary and channel flow model

The model as described in section 3.2.1 together with the inputs calculated as described in the previous section was used to model the flows in the River Tawe during 1976. The only parameter that could be changed in this calibration exercise was the number of lags per reach, N (see section 3.1). The model results seemed very insensitive to variations in N and so it was set to 1 to maximise computational efficiency. The model gave a good agreement with the observed data as shown in figure 3.3

RIVER TAWE STUDY
ESTIMATED AND OBSERVED FLOW AT YNYSTANGLWS
1976



explaining 98% of the variance. The model has been further tested and validated using data for the years 79 and 80 and for the water quality modelling studies the flow model appears satisfactory.

3.3 Modelling Heavy Metals and Suspended Sediments

3.3.1 Model descriptions

The dynamic water quality modelling approach employed in the present studies is based on a continuously stirred tank reactor (CSTR) idealization of a river reach (Figure 3.4). The mathematical formulation of this model is in terms of lumped parameter, ordinary differential equations and draws upon standard elements of chemical engineering reactor analysis (e.g. Himmelblau and Bischoff, 1968). As indicated by Whitehead et al, (1979), this idealization can be shown to approximate the analytical properties of the distributed parameter partial differential equation representations of advection - dispersion mass transport (see Rinaldi et al, 1979) in addition to experimentally observed transport and dispersion mechanisms (Whitehead, 1980). The form of the model has been validated against water quality data in several studies (e.g. Thomann, 1972; Beck and Young, 1976).

The mathematical form of the model is derived from a component mass balance across a reach of river. For the CSTR shown in Figure 3.4:

$$\frac{dx}{dt}(t) \qquad \frac{Q_i(t)}{V} \underline{u}(t) - \frac{Q_o(t)}{V} \underline{x}(t) + \underline{S}(t) \tag{3.6}$$

$\underline{u}(t)$	is the vector of input, upstream component concentrations (mgl^{-1})
$\underline{u}(t)$	is the vector of time-delayed input, upstream component concentrations (mgl^{-1})
$\tau(t)$	is the magnitude of the transportation delay element (day)
$\underline{x}(t)$	is the vector of output, downstream component concentrations (mgl^{-1})
$\underline{S}(t)$	is the vector of component source and sink terms (mgl^{-1} day^{-1})

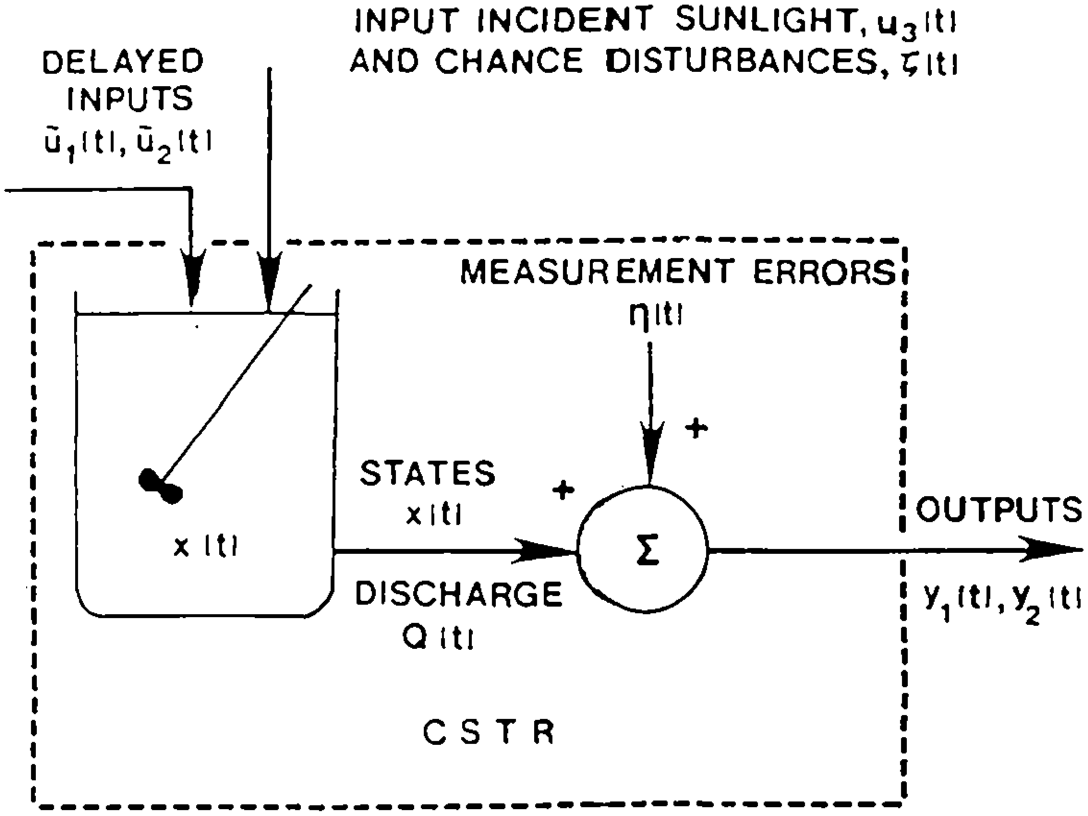


Figure 3.4 Continuously stored tank reactor (CSTR) idealization of a river reach.

$Q_i(t)$ is the upstream discharge (m^3 day^{-1})

$Q_o(t)$ is the downstream discharge (m^3 day^{-1})

is the reach volume (m^3)

is the independent variable of time (days)

This basic mass balance may be modified to suit the nature of the problem and the source/link terms can represent such factors as effluent entering a reach or a chemical decay producing a loss of material down the reach. Integration of the flow and quality models is achieved through the flow term Q occurring in equation (3.6) which is specified at reach boundaries by the flow model.

3.3.2 Application of the model to Heavy Metals and Suspended Sediment in the River Tawe

The model currently simulates Copper, Zinc, Cadmium, Manganese, Iron and suspended sediments. Each of these is modelled in the same way, as a simple mass balance which in its general form can be written mathematically for each compartment as

$$\frac{dx(t)}{dt} \quad \frac{Q_i(t)}{V} \; U_i(t) \quad \frac{Q_o(t)}{V} \; x(t) \quad \frac{Q_G(t)}{V} \; U_G(t) \quad \frac{Q_S(t)}{V} \; U_S(t)$$

$$\frac{Q_T(t)}{V} \; U_T(t) \quad \frac{Q_E(t)}{V} \; U_E(t) \quad \frac{Q_A(t)}{V} \; U_A(t) \quad S'(t) \qquad (3.7)$$

Where the subscripts G,S,T,E and A refer to groundwater inflows surface runoff, tributaries, effluent and abstractions respectively. The term S'(t) represent the combined results of any chemical or physical process that may contribute to the concentrations of a particular metal. This term might include the adsorption of a metal onto suspended sediment or the resuspension of metals under high flows caused by scouring the river bottom. It is also possible that each metal could be considered as being a combination of a particulate and dissolved phase each of which maybe divided into various species of the metal. If this were the case then equations would be written for each of the phases and species and the term S'(t) appearing in each equation would contain terms representing the interaction between the different phases and species. These phases and species might be dependent on such variables as pH or salinity (Forstner and Wittman, 1981).

In the present study only a simple form of the equation has been applied to the River Tawe. No attempt has been made to differentiate between the species of the metals being modelled. The primary object of the modelling study has been to investigate the effect of metal discharges on the River Tawe and how they might relate to the setting of River Quality Objectives (RQO's) or emission standards (ES). The RQO's and ES's set by the European Community are usually stated in terms of concentrations of metals, either dissolved or total, without mention of the species. Thus it is necessary only to produce model results in terms of the sums of all metal species.

As a first attempt at modelling the heavy metals in the River Tawe the model considers only total metal concentrations. Its hoped that the model will be extended to include dissolved metals since European Community RQO's are often stated in terms of dissolved metal concentrations. An examination of the historical data for the River Tawe was undertaken to see if there was any relationship between the measured total and dissolved metal concentrations. As is shown in Table 3.4 some metals show a high correlation coefficient when dissolved concentrations were regressed against total concentrations. The best fits are for Cadmium and Nickel both of which are predominantly in the dissolved form. It maybe possible to use the regression equations for certain of the metals to give an indication of the likely dissolved content given the modelled total concentration.

Since the model considers only total metals and not dissolved metals or metal species, then the term S'(t) in equation 3.7 can only contain information on scouring and sedimentation of metals from or to the river bed. The data set available for calibration of the model was not considered to contain sufficient information to justify including resuspension or scouring terms and so was removed from the model in these initial modelling studies.

Table 3.4

Variable	a parameter	b parameter	correlation coefficient
Cadmium	0.995	0.0	0.99
Copper	0.416	0.003	0.80
Iron	0.059	0.145	0.38
Nickel	0.905	0.001	0.97
Zinc	0.780	0.010	0.88
Manganese	0.582	0.020	0.68

The section of the River Tawe that was modelled had no abstraction plants and was assumed to have no groundwater or direct surface runoff inputs. Thus the mass balance equation for each compartment, equation 3.7 can be simplified to:

$$\frac{dx(t)}{dt} \quad \frac{Q_i(t)}{V} \; U_i(t) \quad \frac{Q_o(t)}{V} \; x(t) \quad \frac{Q_T(t)}{V} \; U_T(t) + \frac{Q_e(t)}{V} \; U_e(t)$$

where the variables have the same meaning as in equation 3.

The data used to calibrate the model was from the 5-week survey carried out by the Institute of Hydrology between 26 October 1982 and 29 November 1982. This survey provided daily values of the modelled variables at the upstream end of the catchment and for the major metal inputs to the Tawe, with the exception of the INCO effluent at Clydach. No daily data for the INCO effluent was available for this period and for the purpose of the modelling study a mean value for the effluent was used, taken from the consent conditions imposed by the Welsh Water Authority. The survey also provided daily concentrations of heavy metals and other water quality variables at four sites in the modelled section. A detailed description of the 5-week survey can be found in a previous report to the European Commission (Whitehead et al, 1984).

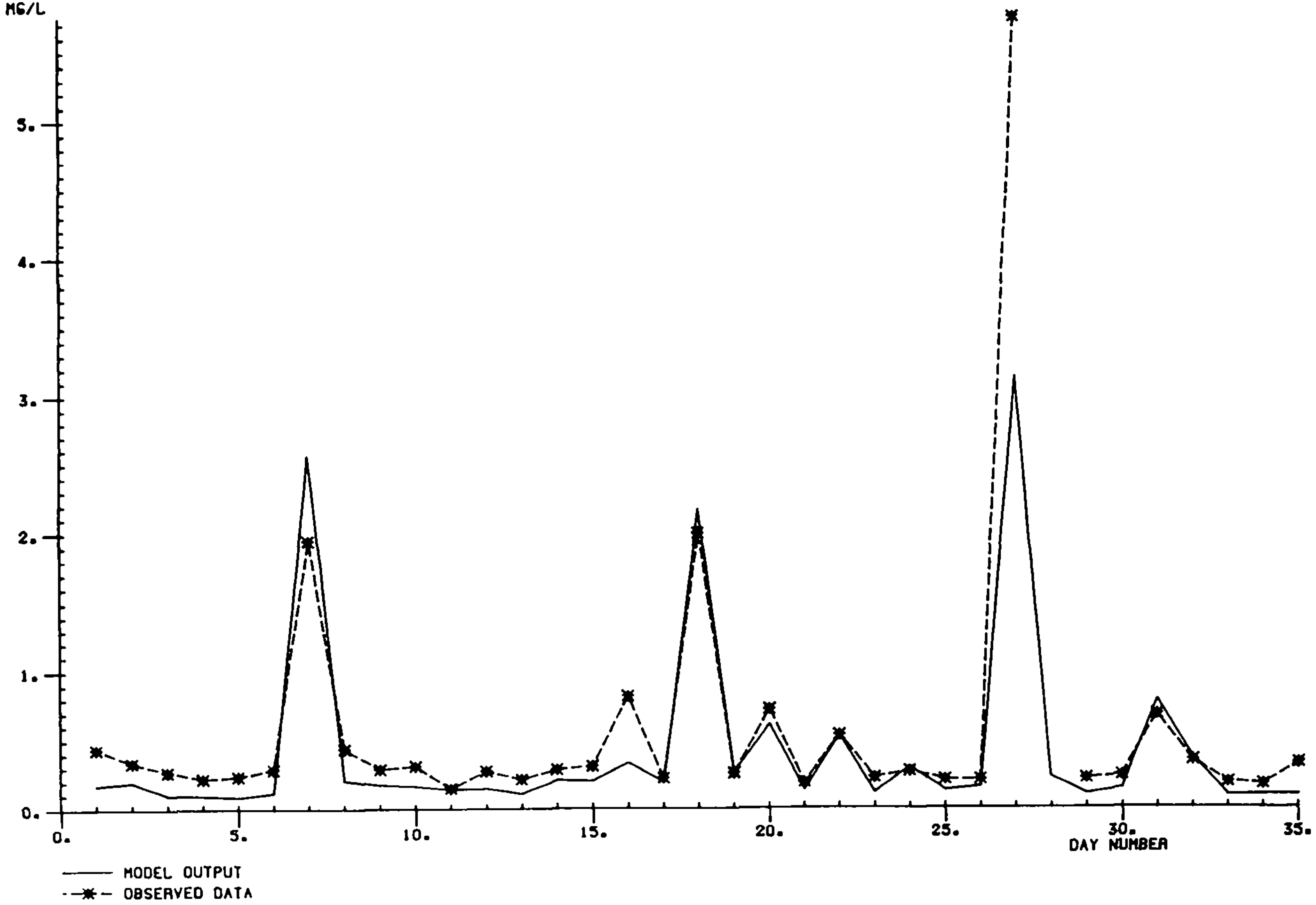
The ability of the model to fit the data collected over the 5-week survey varied, from metal to metal and from site to site. The best fit to the data was for Iron, figures 3.5 and 3.6 show observed and simulated iron concentrations at Ynystanglws and Morriston respectively. The effluent from the British Steel Corporation works at Velindre enters the Tawe between Ynystanglws and Morriston but does not increase the Iron levels significantly under the prevailing, average to high, flow conditions. The Velindre effluent also contains high levels of manganese. Figures 3.7 and 3.8 show observed and simulated manganese concetrations at Ynystanglws and Morriston respectively. Once again little increase in concentrations is found as a result of the Velindre effluent. The model does, however, predict small peaks of manganese at Morriston, not found in the observed data, that are coincident with high manganese concentrations on the Velindre effluent. Despite this the model gives reasonable estimates of the observed data.

The effluent from the INCO nickel works contains nickel and copper quite high concentrations the mean values being 1.3 mg/l and 0.1 mg/l respectively. This effluent has a marked effect on the concentrations downstream of the effluent. Figures 3.9 and 3.10 show observed and simulated nickel concentrations at Glais and Ynystanglws respectively. The model gives poor estimates of the observed nickel at Glais, whic in part be due to the fact that these values are at or about the lim detection used in the chemical analysis. The model gives a good est of the peak on days 18 and 19 but misses the peaks on days 10 and 1 model also estimates a peak on day 32 not shown in the observed data, coinciding with a high nickel concentration at Pontardawe the upstre of the modelled section.

At Ynystanglws the model shows a marked improvement in its abil to estimate the observed nickel. The modelled output does not exhibit much variation from day to day as the observed data, this is probably to the use of a mean value for the nickel concentration in the INCO effluent. If the daily data for the effluent were available this wo improve the performance of the model.

The model results for copper at Glais and Ynystanglws are shown figures 3.11 and 3.12 respectively. The model does not estimate the

RIVER TAWE STUDY
IRON AT YNYSTANGLWS



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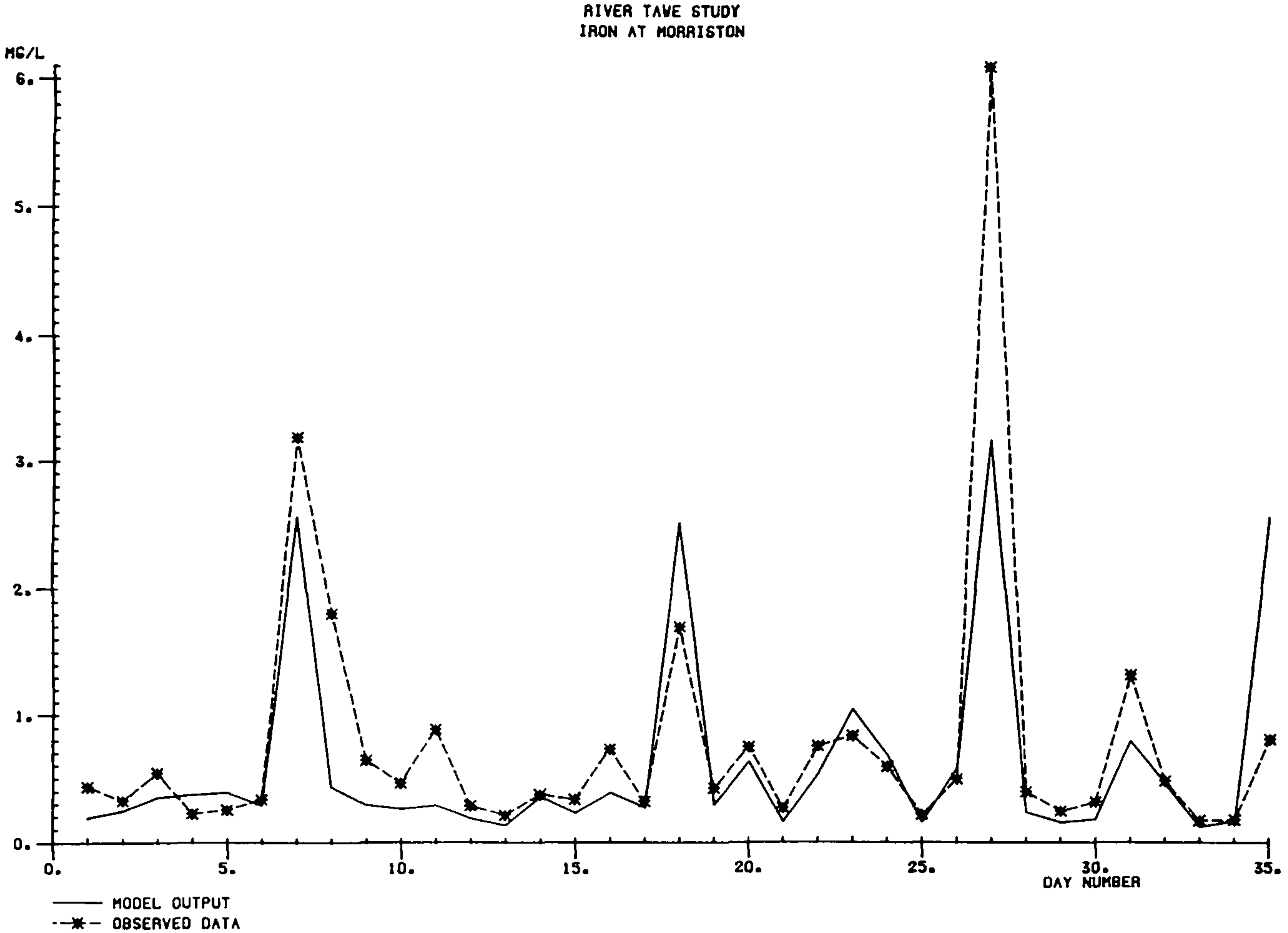

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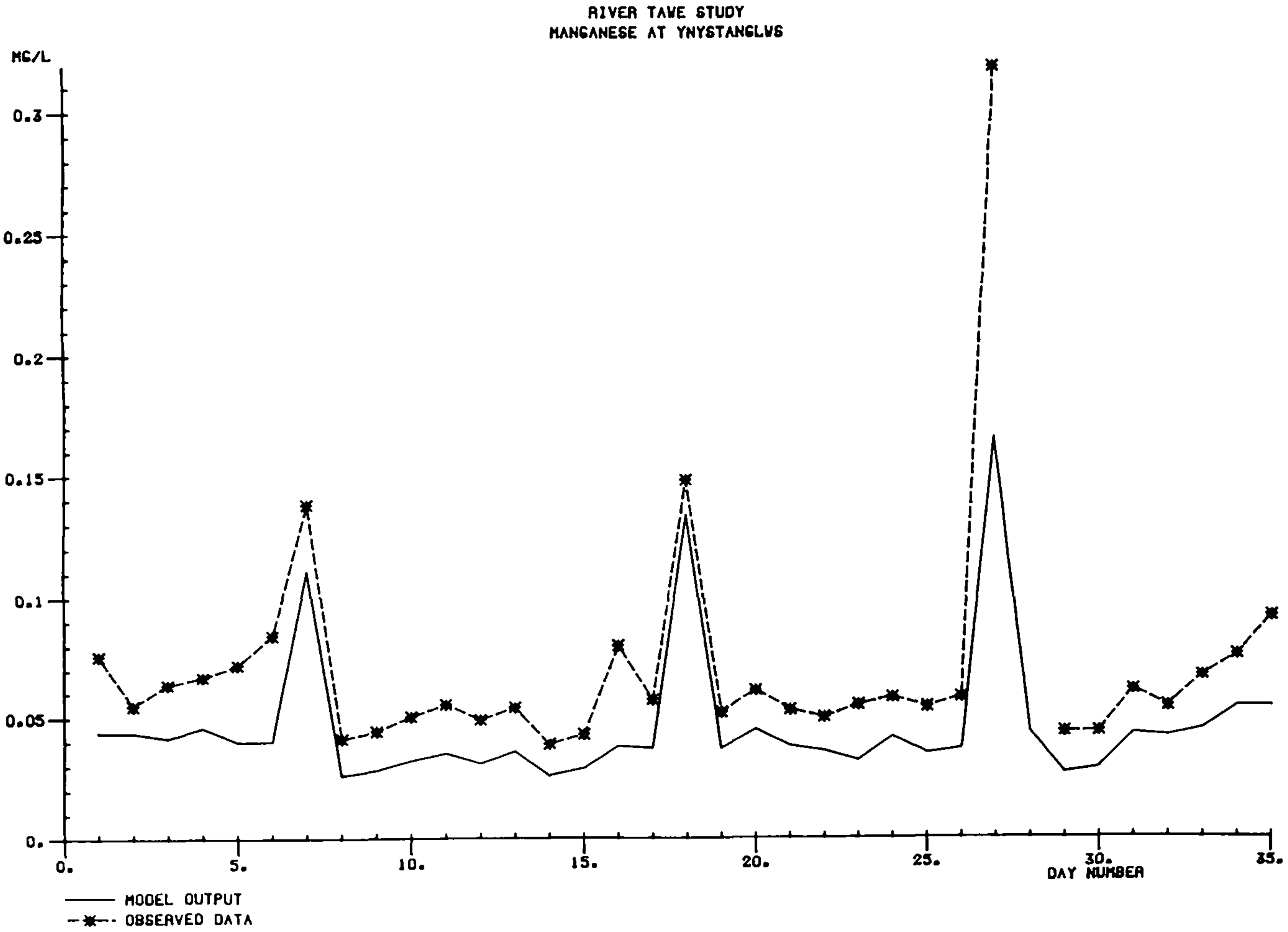
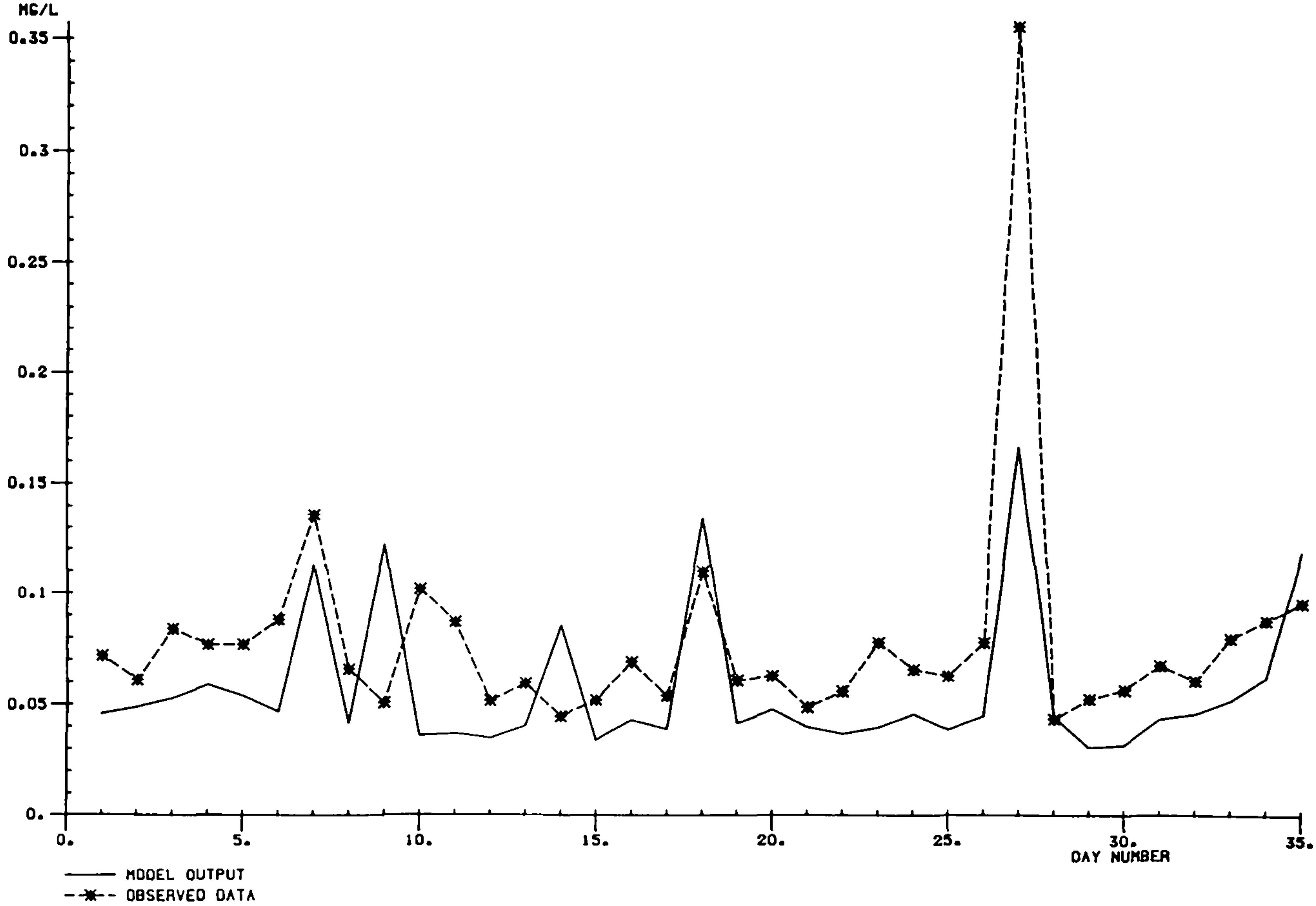


Figure 3.7 Observed and simulated daily Manganese concentrations at Ynystanglws from 26 October - 29 November 1982.

RIVER TAWE STUDY
MANGANESE AT MORRISTON



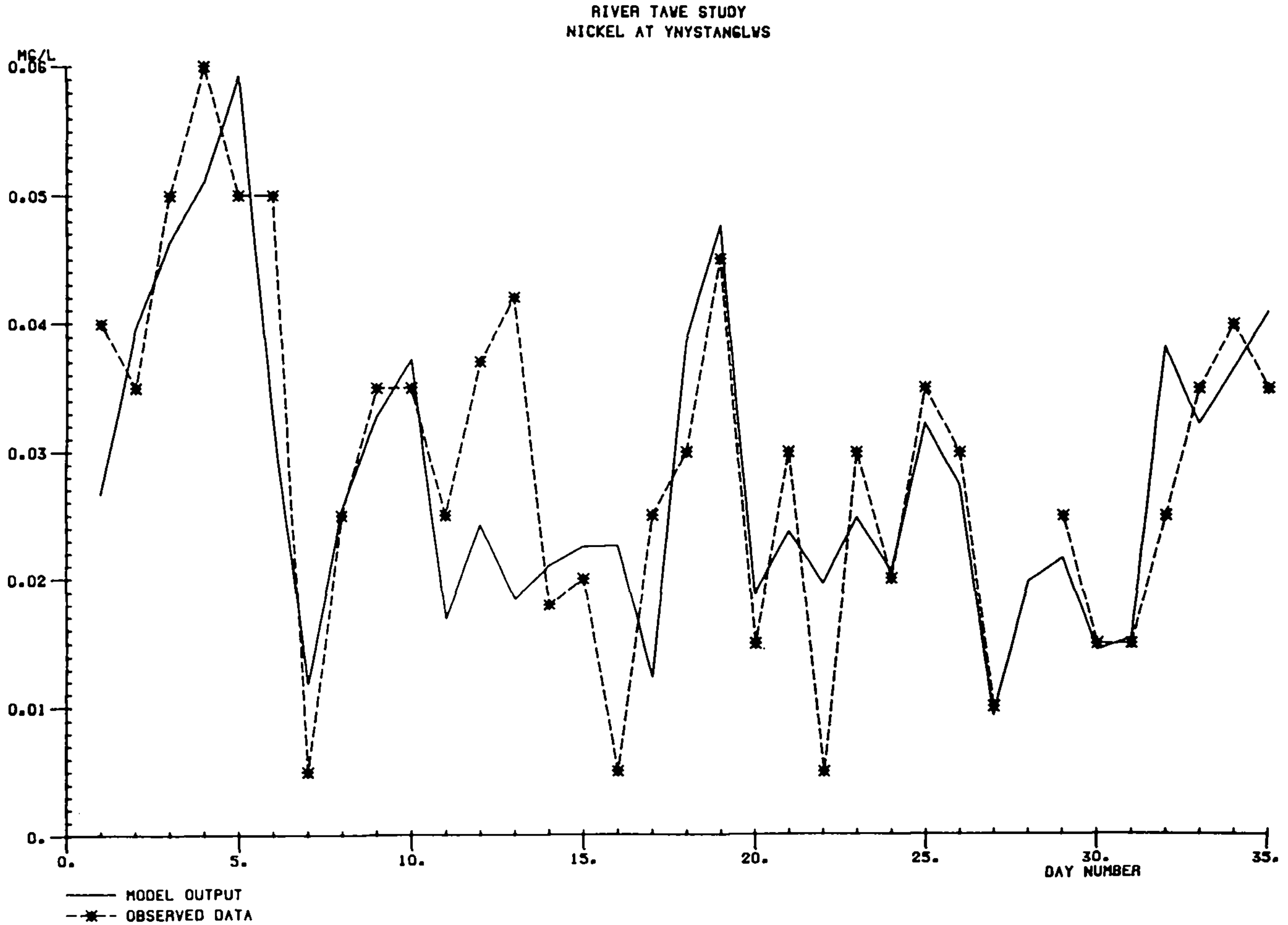
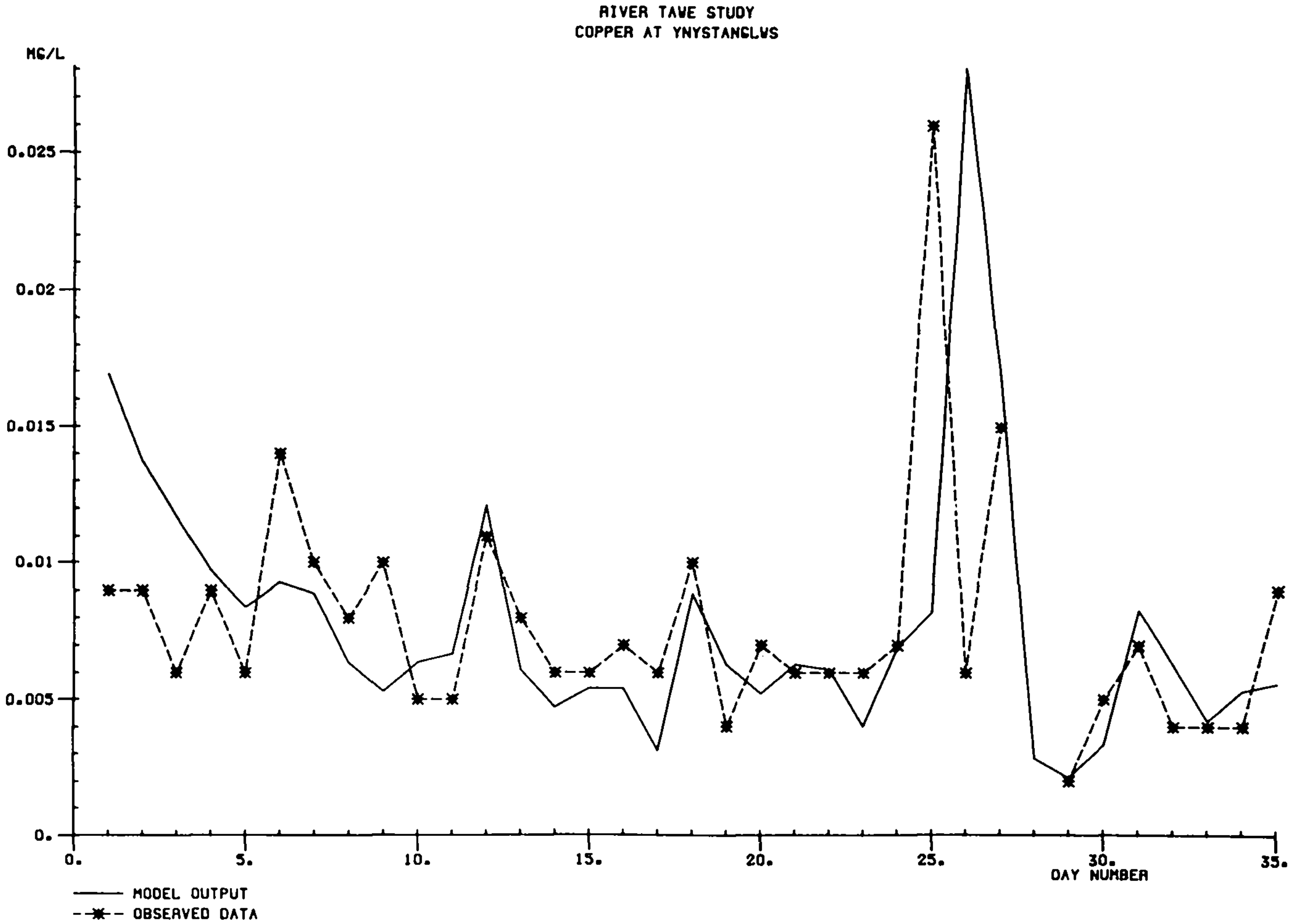


Figure 3.9 Observed and simulated daily Nickel concentrations at Ynystanglws from 26 October - 29 November 1982.



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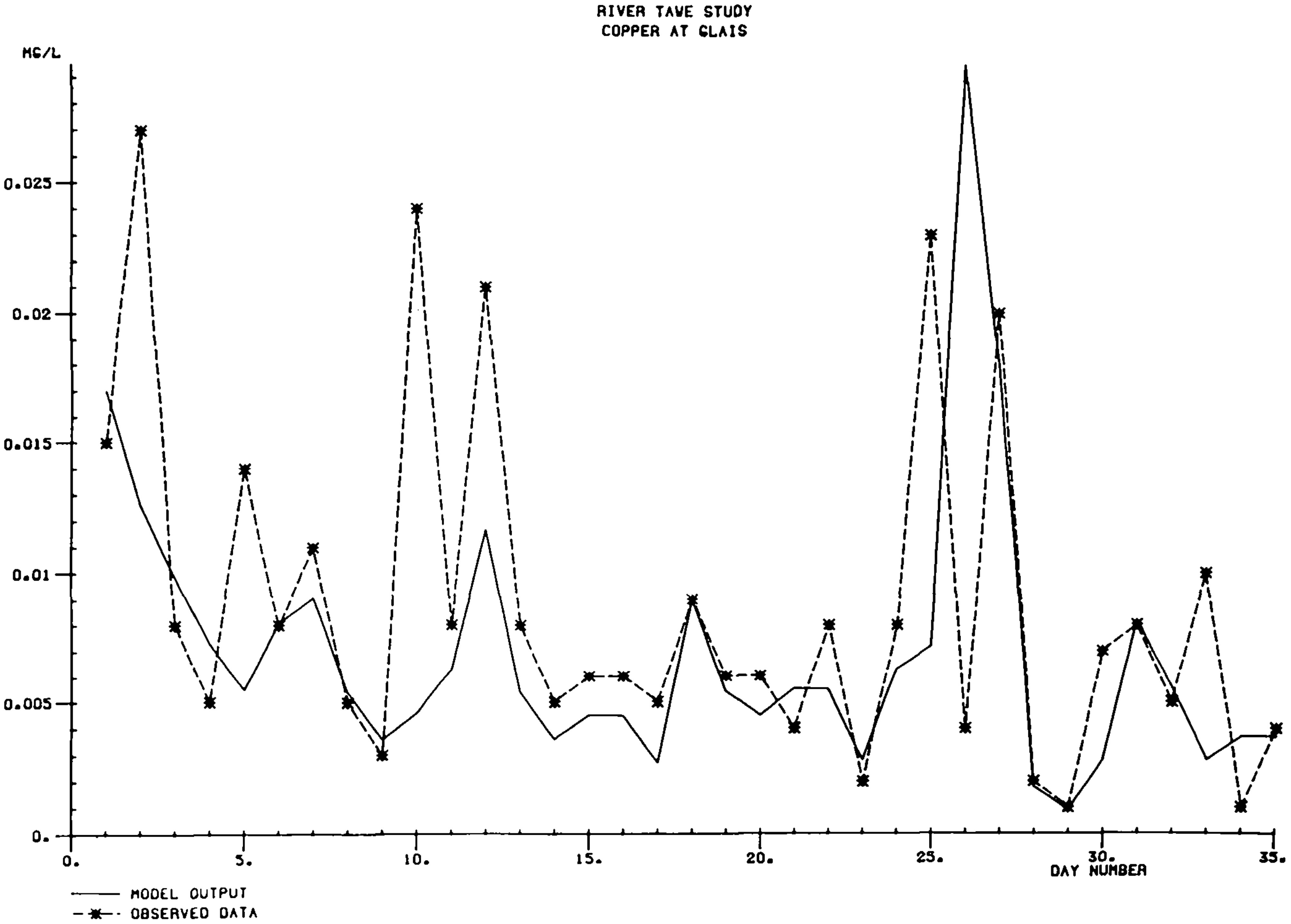

Figure 3.12 Observed and simulated daily Copper concentrations at Glais from 26 October - 29 November 1982.

variations in the copper levels very well but does, at least, estimate the general levels quite well. It can be seen from these results that under the prevailing hydrology of average to high flows the INCO effluent has very little effect on the concentrations in the receiving rivers.

The modelled concentrations of cadmium and zinc are most affected by the Nant-y-Fendrod, a tributary of the Tawe, that enters the river between Morriston and Landore. The Nant-y-Fendrod drains from an area covered in old waste dumps created by the metal smelting industries in the Lower Swansea Valley. These tips are high in metals which are leached out into the Nant-y-Fendrod thus making it a major metal source into the Tawe. Table 3.5 gives a summary of the data from the Nant-y-Fendrod collected during the 5-week survey.

Table 3.5 Summary of Nant-y-Fendrod data (mg/l)

Metal	**Copper**	**Zinc**	**Cadmium**	**Manganese**	**Iron**	**Nickel**
Maximum	0.088	8.0	0.046	1.3	7.25	0.04
Minimum	0.006	0.022	0.001	0.29	0.4	0.01
Mean	0.02	3.52	0.019	0.66	1.54	0.015
Standard Deviation	0.016	2.02	0.011	0.2	1.45	0.007

The data collected during the 5-week survey showed inconsistencies for both cadimum and zinc particularly at the Morriston and Landore sampling sites. These inconsistencies cannot easily be explained but they may have been caused by an unidentified direct runoff from the metal bearing tips, resuspension of muds or even cross contamination from the sampling of the highly metal bearing Nant-y-Fendrod.

Despite the reservations about the daily simulation model there is no reason why a preliminary application of the model should not be undertaken. A suitable subject for this is the effect of effluent discharges on 95 percentile concentrations of metals in the river and how these change under differing hydrological condition. A model application of this type has been undertaken and is described in the next section.

A PRELIMINARY APPLICATION OF THE HEAVY METAL MODEL FOR THE RIVER TAWE

As a first model application an investigation was carried out on the effects of effluent discharges on river water quality under different hydrological conditions. This involved selecting three recent years each reflecting different hydrology and running daily simulations for each of these years. Output from the model was obtained for four sites on the river for each of the three years 1976, 1979 and 1980 in the form of a fractional cumulative frequency curve of concentrations for each of the modelled variables. In this way it is possible to look at the changes in the 95 percentile value, i.e. the value of the concentration that 95% of the calculated concentrations are below. It is important to characterize the results in this way since the EEC guidelines for effluent standards and river quality objectives are most frequently stated in these terms.

4.1 Estimation of Water Quality Inputs

The major metal inputs to the model come from two different sources, 'natural*' and man-made. The two 'natural' sources are the River Tawe at

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* *'Natural' in this sense refers not to the original source of the metal but to the means by which is enters the river, i.e. via a tributary and not an effluent pipeline.*

the upstream end of the modelled section, Pontardawe, and the Nant-y-Fendrod. There are three man-made inputs, Trebanos Sewage Treatment Works, INCO Nickel Works and Velindre Steel Works. Daily data does not exist for these inputs for the years selected and so they must be estimated.

The 'natural' inputs were estimated by regressing log load against log flow for each model variable using all the available routinely collected data from the period 1977 to 1982. This gave a relationship of the form

$$= bQ^a \qquad (4.1)$$

where L is the load of a particular variable (g/s), Q is the flow rate (cumecs) and a and b are the parameters from the regression. Table 4.1 gives the values of a and b for each of the model variables for the two natural inputs together with the correlation coefficient for each equation.

Table 4.1 Parameters for the Flow-load Relationships

	Tawe at Pontardawe			Nant-y-Fendrod		
Variable		b	correlation coefficient		b	correlation coefficient
Suspended solids	1.25	2.93	0.87	2.42	2.83	0.77
Iron	1.55	0.065	0.92	0.90	1.13	0.80
Copper	1.10	0.004	0.88	1.05	0.018	0.87
Zinc	1.41	0.012	0.92	0.74	3.44	0.59
Nickel	1.24	0.003	0.93	1.00	0.020	0.89
Manganese	1.28	0.022	0.95	0.75	0.80	0.78
Cadmium	1.10	0.0007	0.86	0.73	0.034	0.62

The regressions for Pontardawe gave very good fits in all cases and can be considered to give good estimates of the input variables. The regressions for the Nant-y-Fendrod were not so good but on the whole are acceptable with perhaps the exception of zinc and cadmium. Although the Nant-y-Fendrod is the major zinc source in the River Tawe, this lack of a good definition of this source is not important at the present since this model application is concerned mainly with the man-made effluents entering the river.

The man-made effluent inputs to the river were estimated by assuming that the concentrations would be log normally distributed and hence each effluent is represented by a mean and standard deviation. The value of the concentration to be used each day is taken at random from the distribution so defined. The means and standard deviations used for each of the effluents for each model variable are given in Table 4.2.

Table 4.2 **Mean and Standard Deviations of the main effluents**

		S.S	Copper	Zinc	Cadmium	Manganese	Iron	Nickel
TRENBANOS EFF	MEAN	7.2000	0.011	0.028	0.0030	0.069	0.209	0.0128
	SD	2.7000	0.0065	0.0021	0.0027	0.026	0.214	0.0046
INCO EFF	MEAN	10.000	0.100	0.	0.	0.	0.	1.380
	SD	4.000	0.030	0.	0.	0.	0.	0.500
VELINDRE EFF	MEAN	22.10	0.016	0.240	0.001	1.100	10.70	0.011
	SD	47.00	0.018	0.710	0.001	1.800	17.20	0.017

To ensure a fair comparison between the different runs the values of the effluent discharge parameters were left unchanged from year to year. In order to ensure they were of the right order of magnitude, however, the values collected during the 5-week survey were used. This was not possible for the INCO effluent so the latest consent values as stipulated by the Welsh Water Authority were used.

Three different types of hydrology were chosen to represent 'wet', 'dry' and 'average' years. Using the annual mean flow as the criteria 1976 was chosen to represent a dry year, 1979 to represent a 'wet' year and 1980 to represent an 'average' year. The hydrographs for the three chosen years are shown in figure 4.1. The few flows in excess of 75 cumecs have been cut-off the top of the graphs to allow better definition of the rest of the hydrograph.

4.2 Effects of Effluent Discharges on River Water Quality

The effluent from the INCO nickel works at Clydach enters the River Tawe between the model output locations of Glais and Ynystanglws. The effect of this effluent can clearly be seen in figure 4.2 where the distribution of Nickel concentrations has been shifted dramatically up the scale. The 95 percentile has changed from 0.005 mg/l at Glais to 0.3177 mg/l at Ynystanglws, an increase of more than 50 fold. The mean Nickel concentration has also increased from 0.0046 mg/l to 0.0970 mg/l this represents an increase of more than 24 fold. The only other metal affected by the INCO outfall is copper (figure 4.3). For this case there is an increase in the 95 percentile from 0.0056 mg/l to 0.0293 mg/l and an increase in the mean from 0.0049 mg/l to 0.0113 mg/l.

The effluent from the British Steel Works at Velindre enters the River Tawe between Ynystanglws and Morriston. This effluent has most effect on the concentrations of Manganese, Cadmium and Iron as shown in figures 4.4, 4.5 and 4.6.

The 95 percentile value for Manganese increases from 0.046 mg/l to 0.196 mg/l and the mean changes from 0.0[illegible] to 0.083 mg/l. The increase in the 95 percentile value for Cadmium is from 0.0011 mg/l to 0.0045 mg/l and the mean increase from 0.008 mg/l to [illegible]17 mg/l. There is a large increase in the Iron 95 percentile concentration from 0.344 mg/l to 1.529 mg/l and the mean value increases from 0.116 mg/l to 0.523 mg/l.

The results given above indicate that [illegible] industrial discharges into the River Tawe do make a significant contribution to its heavy metal load. There is, however, another source of metals from the Nant-y-Fendrod a tributary of the Tawe which enters the river between Morriston and Landore. This tributary affects the concentrations of Manganese, Cadmium and Zinc as shown in figures 4.4, 4.5 and 4.7. The 95 percentile value

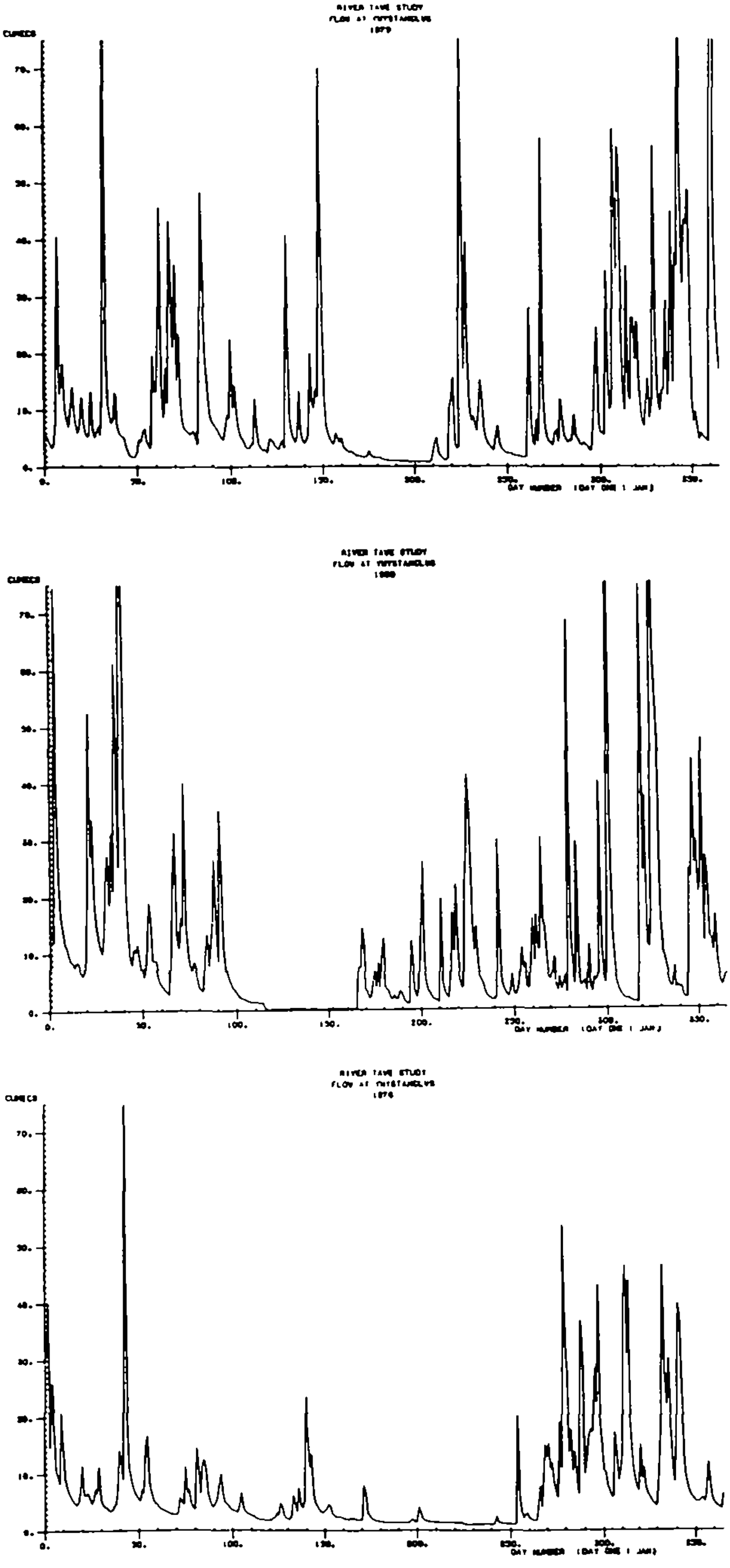


Figure 4.1 Recorded flows at Ynystanglws for 1976, 1979 and 1980.

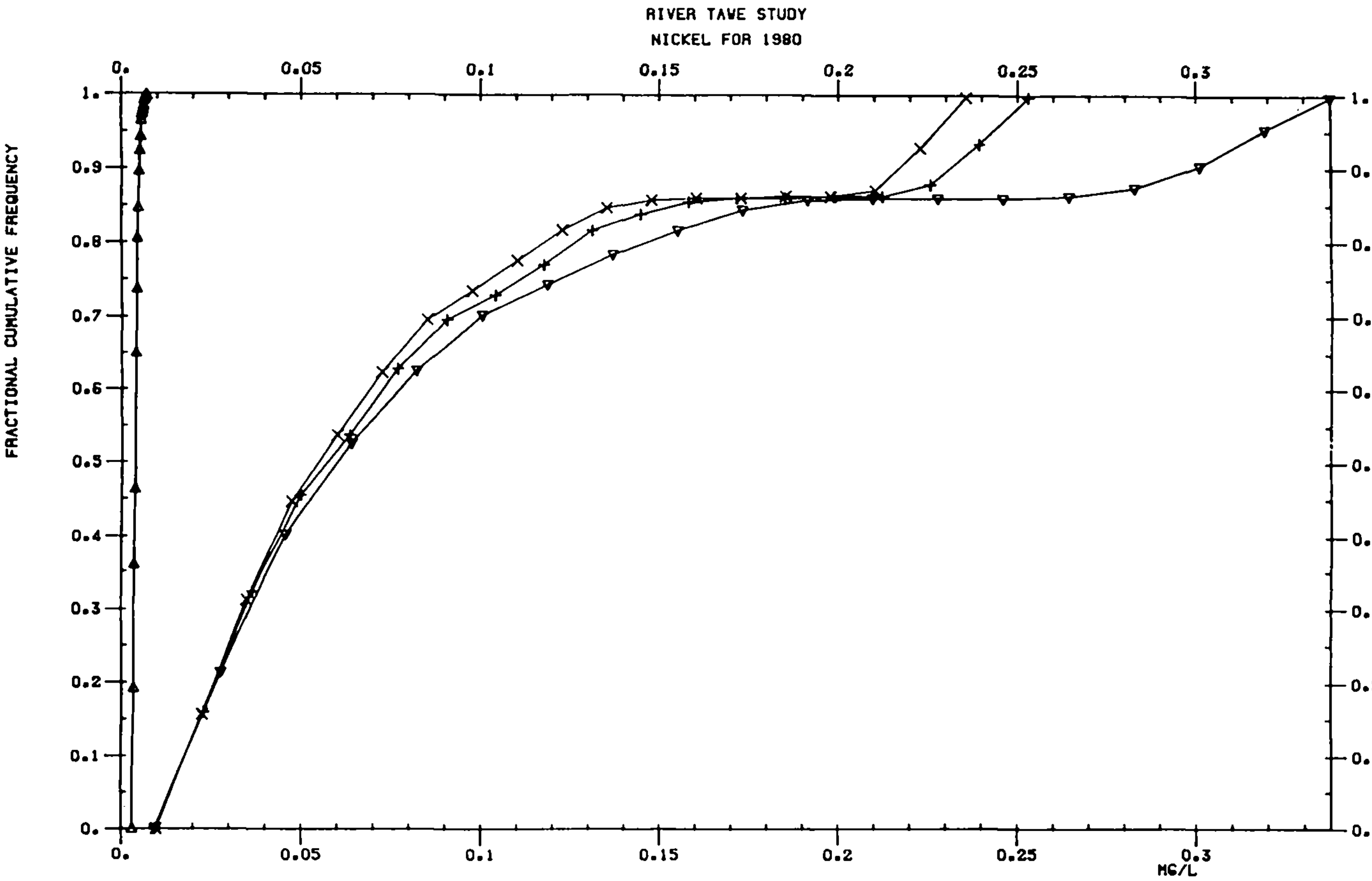


Figure Simulated cumulative frequency curves for Nickel at four sites on the River Tawe for 1980.

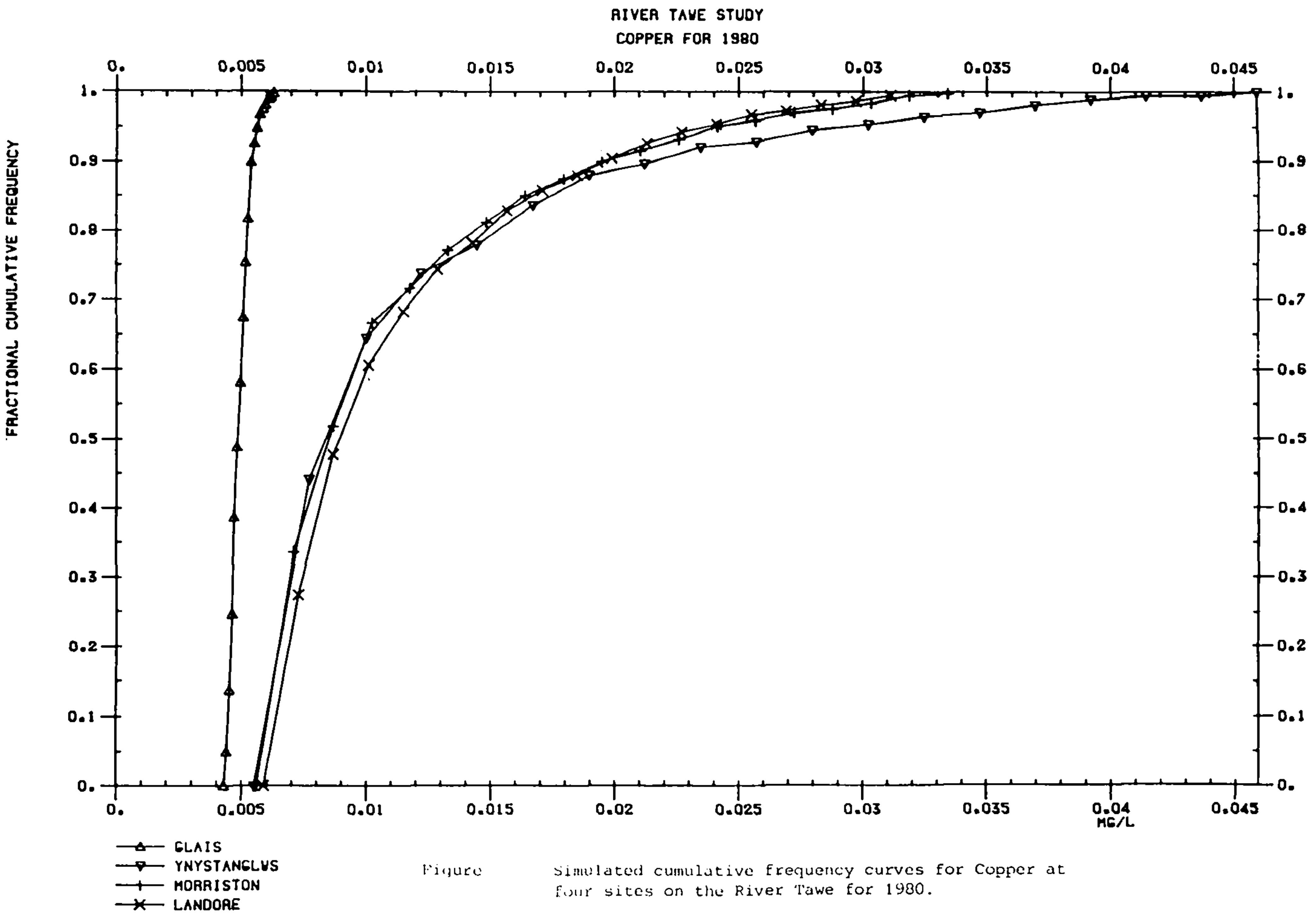
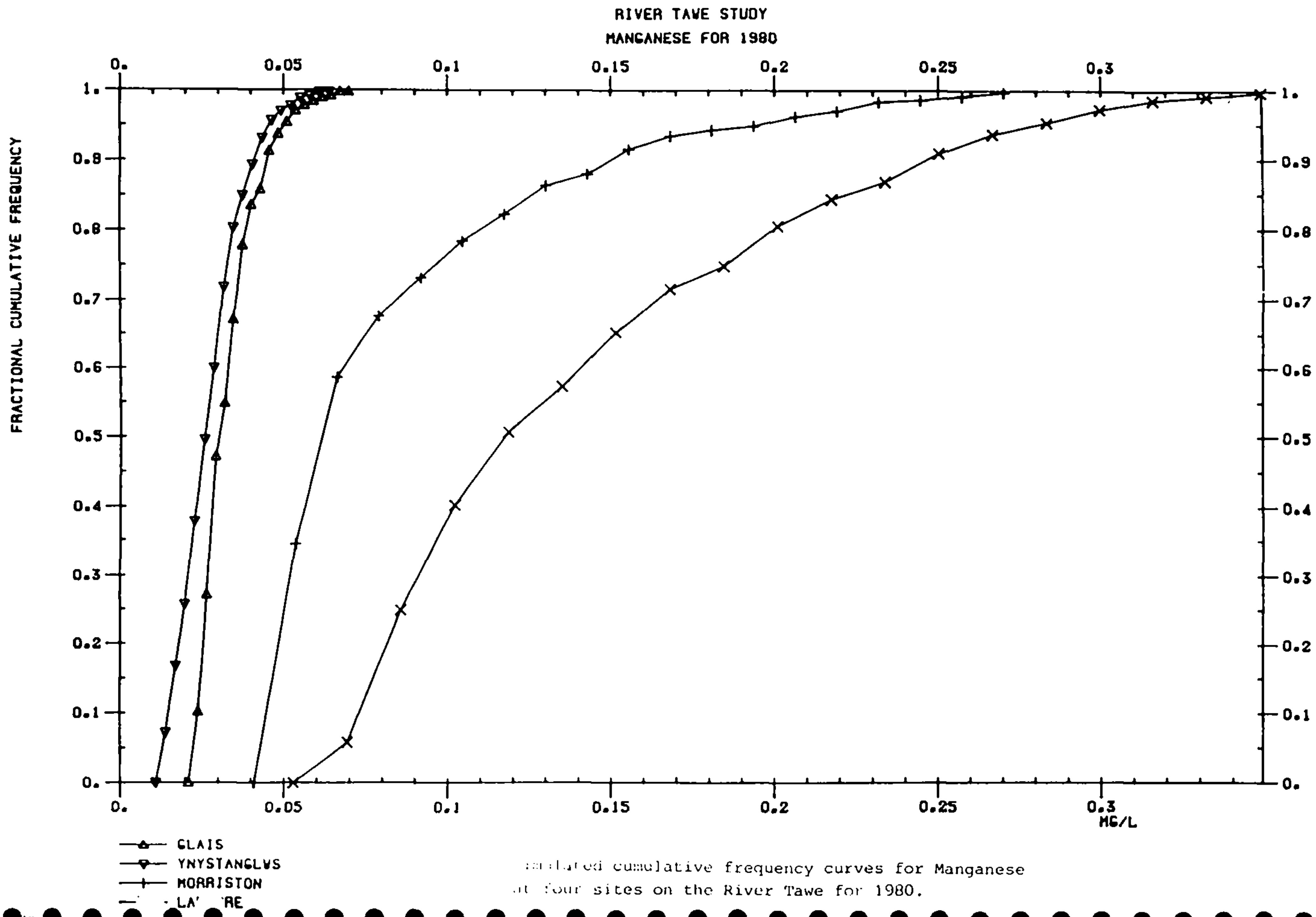


Figure Simulated cumulative frequency curves for Copper at four sites on the River Tawe for 1980.



lated cumulative frequency curves for Manganese
at four sites on the River Tawe for 1980.

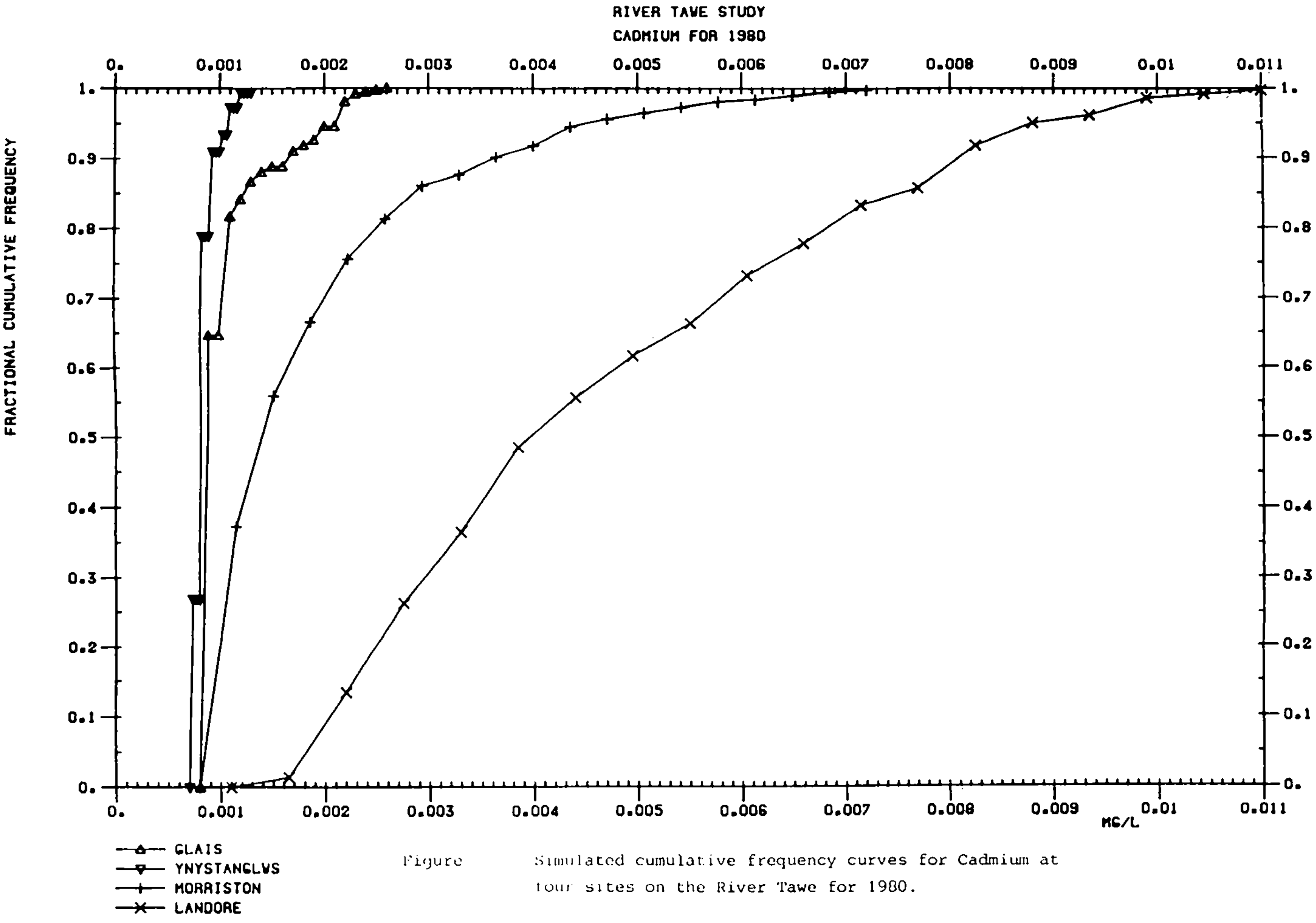
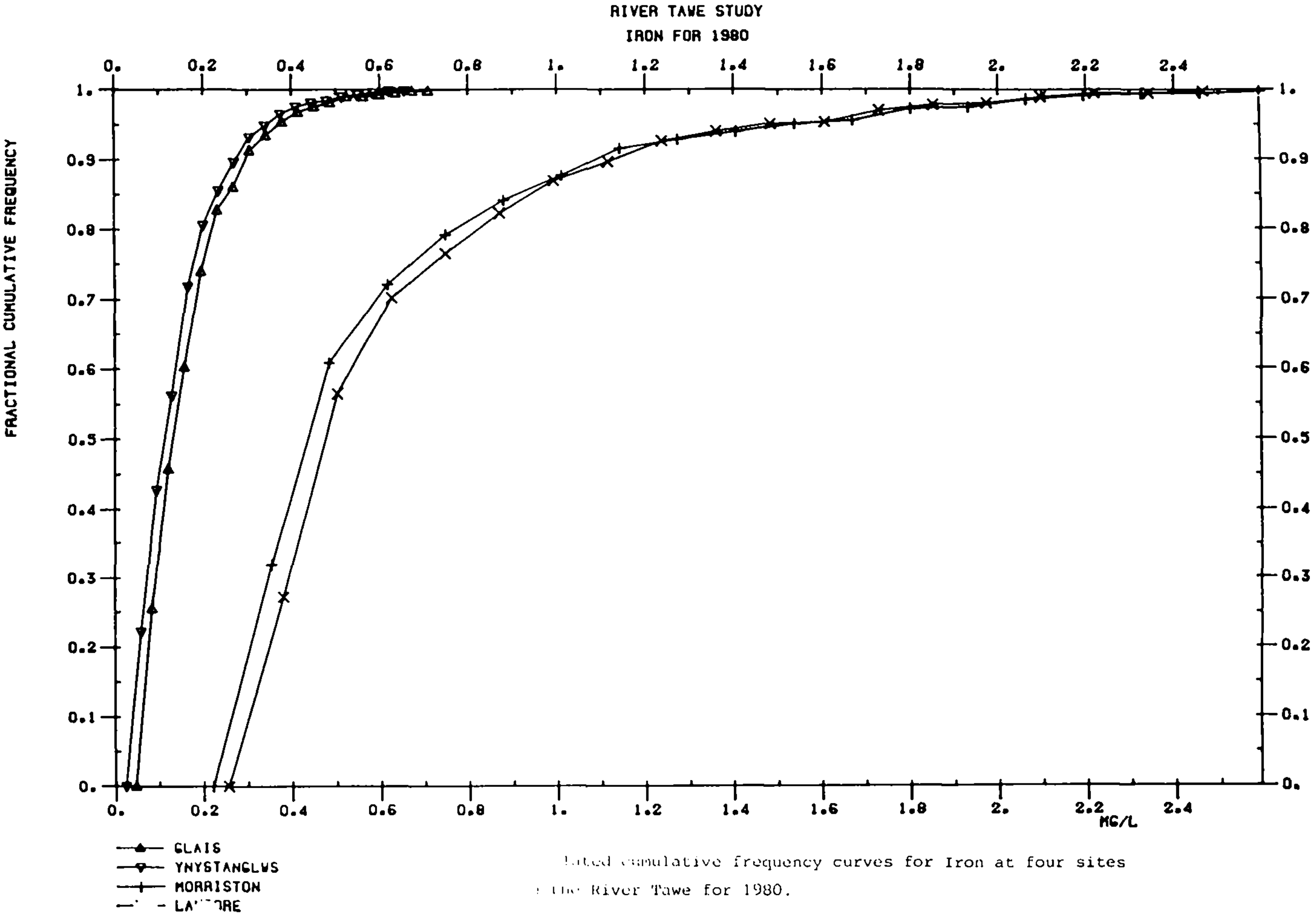


Figure Simulated cumulative frequency curves for Cadmium at four sites on the River Tawe for 1980.



lated cumulative frequency curves for Iron at four sites

the River Tawe for 1980.

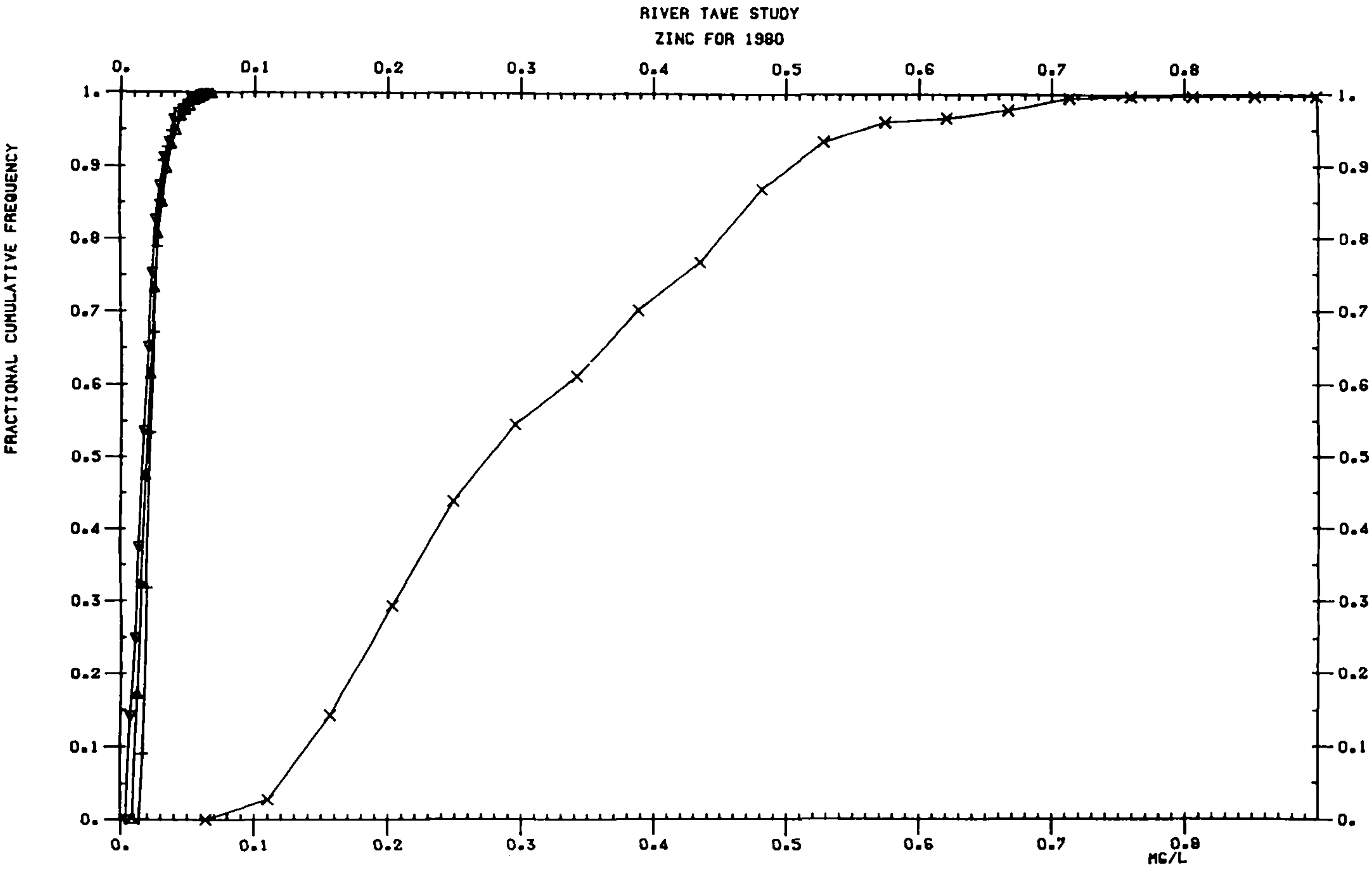


Figure 4 7 Simulated cumulative frequency curves for Zinc at four sites on the River Tawe for 1980.

for Manganese increased from 0.196 to mg/l to 0.280 mg/l and the mean from 0.083 mg/l to 0.142 mg/l. The 95 percentile value for Cadmium almost doubled from 0.0045 mg/l to 0.0088 mg/l and the mean more than doubled from 0.0019 mg/l to 0.0046 mg/l. The Nant-y-Fendrod is the major source of Zinc to the Tawe and its affect on the 95 percentile is to increase it by more than ten times from 0.0388 mg/l to 0.5546 mg/l with a similarly large increase in the mean from 0.024 mg/l to 0.309 mg/l.

4.3 The effect of Effulents on River Water Quality under different hydrological conditions

The first part of the investigation has indicated the locations mostly affected by the effluents and it is now possible to look at the influence that different hydrological conditions have on the concentration distributions at these locations. As was described earlier the year 1976, 1979 and 1980 were chosen, an the basis of mean annual flow, to represent 'dry' 'wet' and 'average' years respectively.

At the locations where the metal concentrations are affected by the industrial effluent sources the same pattern of results was evident for almost all of the metals for the three years considered. In all of these cases the 95 percentile concentration is highest in the 'average' year of 1980 and lowest was the 'wet' year of 1979 while the 'dry' year of 1976 comes inbetween, (Figures 4.8, 4.9, 4.10. For example is figure 4.. the 95 percentile Iron concentrations at Morriston was 1.53 mg/l for the 'average' year of 1980, 1.19 mg/l for the 'dry' year of 1976 and 1.04 for the 'wet' year of 1979. The one exception to this was Nickel at Ynystanglws (figure 4.12). The 95 percentile value for 1980 was still the highest at 0.32 mg/l, but this time the 'wet' year of 1979 had the next highest value at 0.19 mg/l and the dry year of 1976 had the lowest value at 0.17 mg/l.

The mean metal concentrations also show the same ranking over the three years of 1980 as the highest, 1979 as the lowest and 1976 between these two. Table 4.3 contains a summary of the means, standard deviations and 95 percentile values for each of the metals at selected sites.

Table 4.3 Means, standard deviations and 95 percentile values for the metals at three sites for 1976, 1979 and 1980 (Mg/1)

Morriston

	Cadmium			Manganese			Iron		
	1976	1979	1980	1976	1979	1980	1976	1979	1980
Mean	0.0017	0.0015	0.0019	0.075	0.068	0.083	0.53	0.48	0.57
S.D.	0.0008	0.0007	0.0012	0.030	0.026	0.051	0.29	0.24	0.40
95%	0.0032	0.0028	0.0045	0.142	0.130	0.200	1.19	1.04	1.53

Ynystanglws

	Copper			Nickel		
	1976	1979	1980	1976	1979	1980
Mean	0.0104	0.0093	0.0113	0.083	0.068	0.097
S.D.	0.0045	0.0041	0.0076	0.050	0.050	0.095
95%	0.0198	0.0177	0.0343	0.172	0.186	0.318

Landore

	Zinc		
	1976	1979	1980
Mean	0.272	0.249	0.309
S.D.	0.142	0.095	0.147
95%	0.567	0.424	0.555

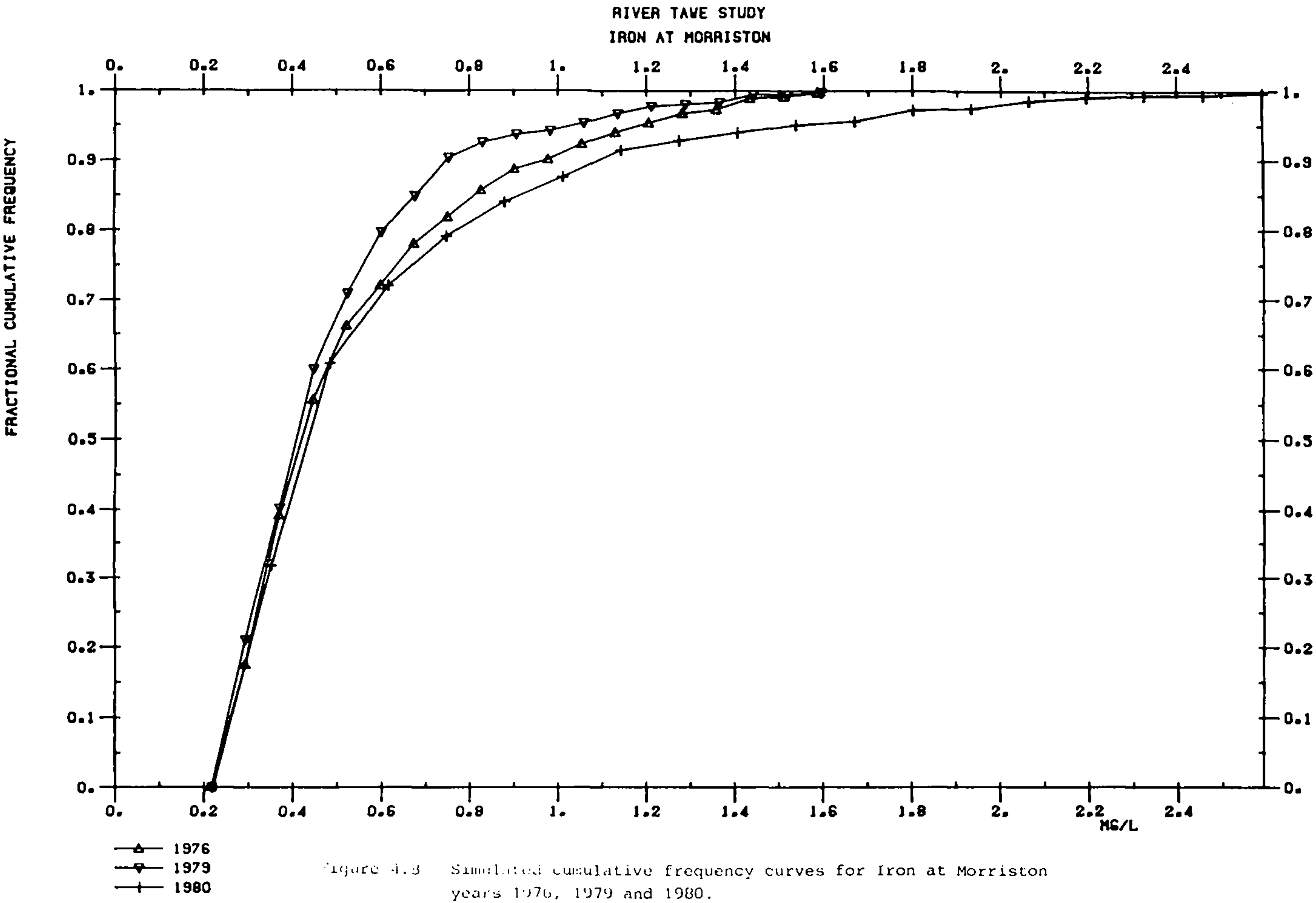
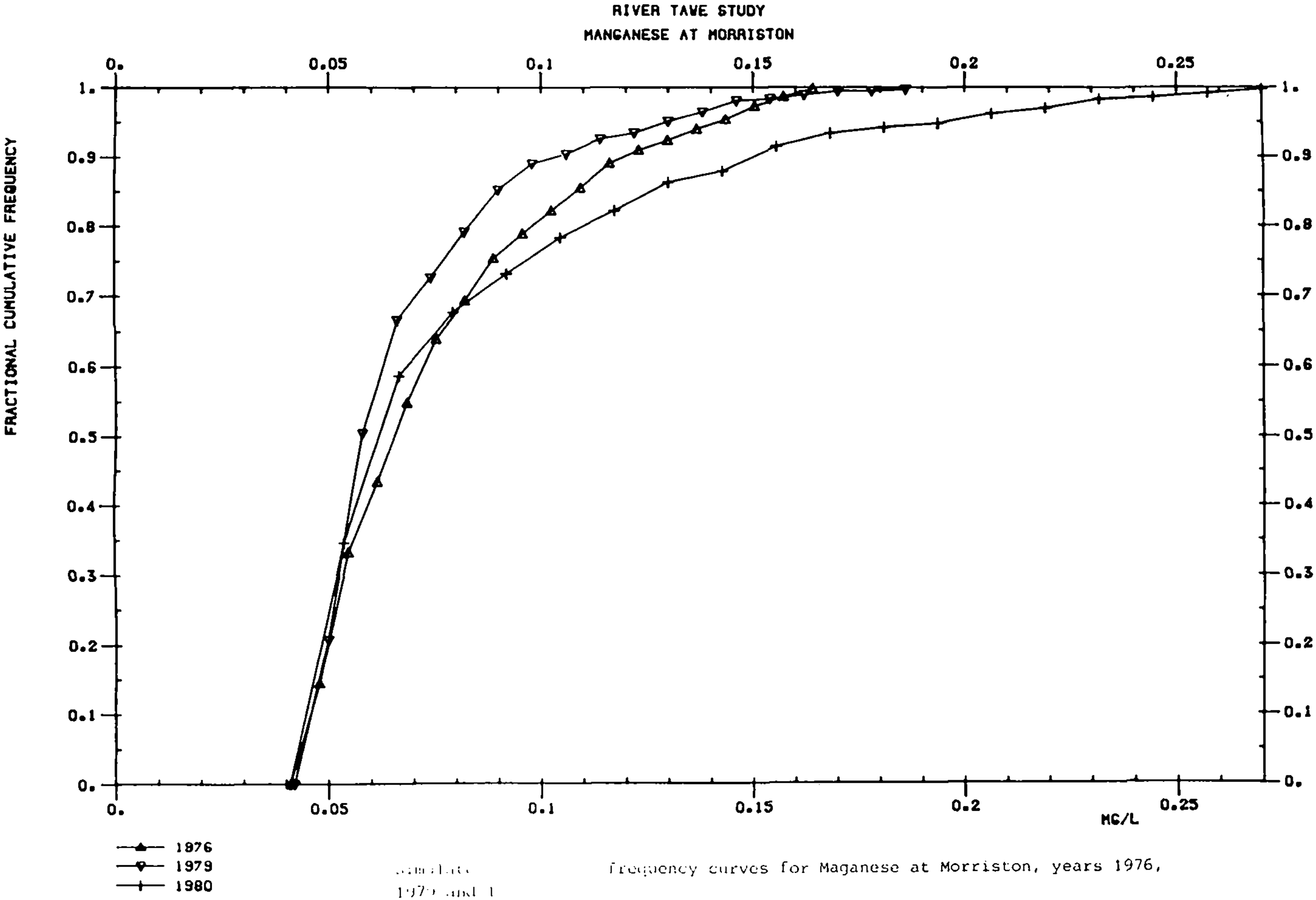


Figure 4.3 Simulated cumulative frequency curves for Iron at Morriston years 1976, 1979 and 1980.



umulative Frequency curves for Maganese at Morriston, years 1976,
1979 and 1

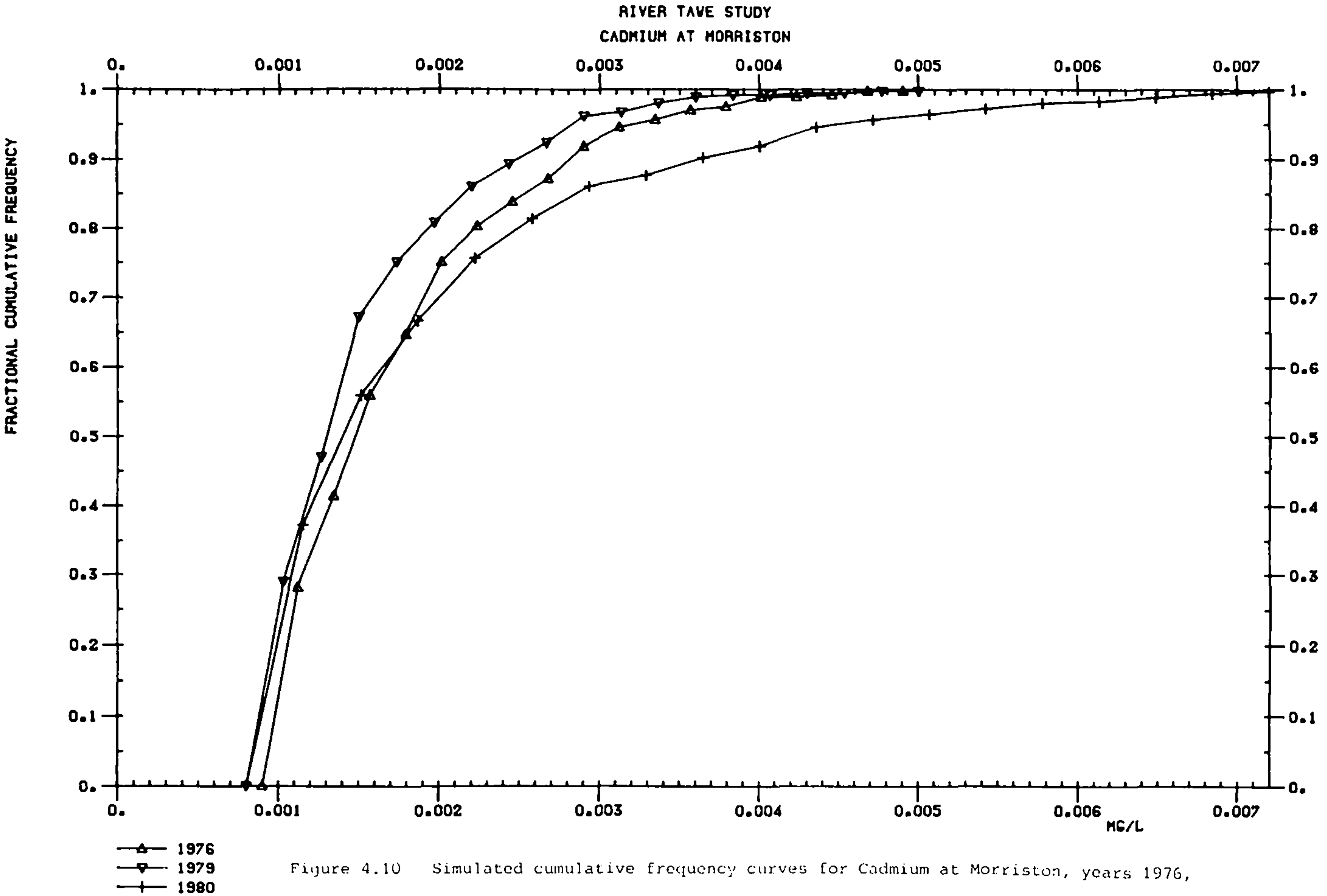


Figure 4.10 Simulated cumulative frequency curves for Cadmium at Morriston, years 1976, 1979 and 1980.

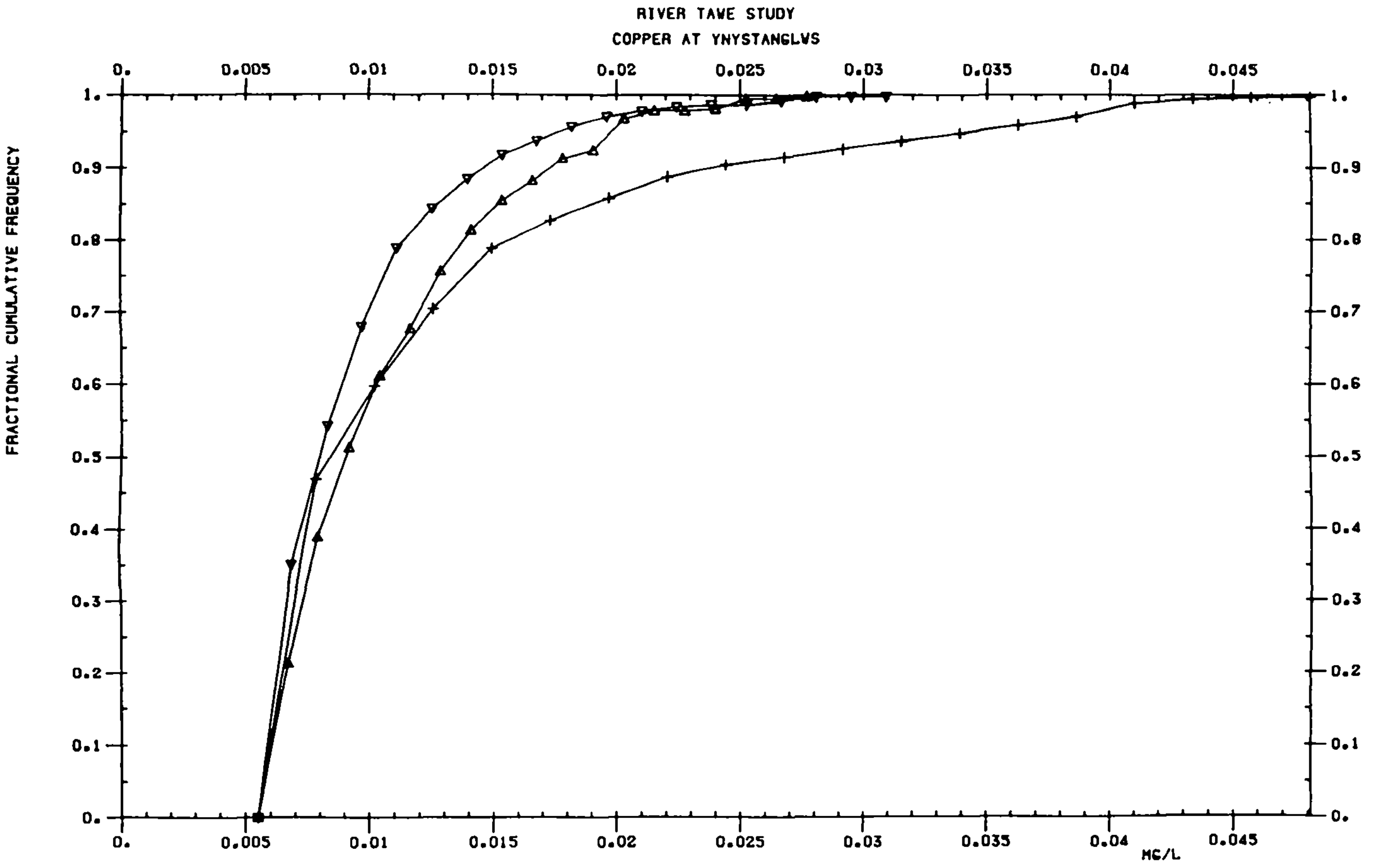
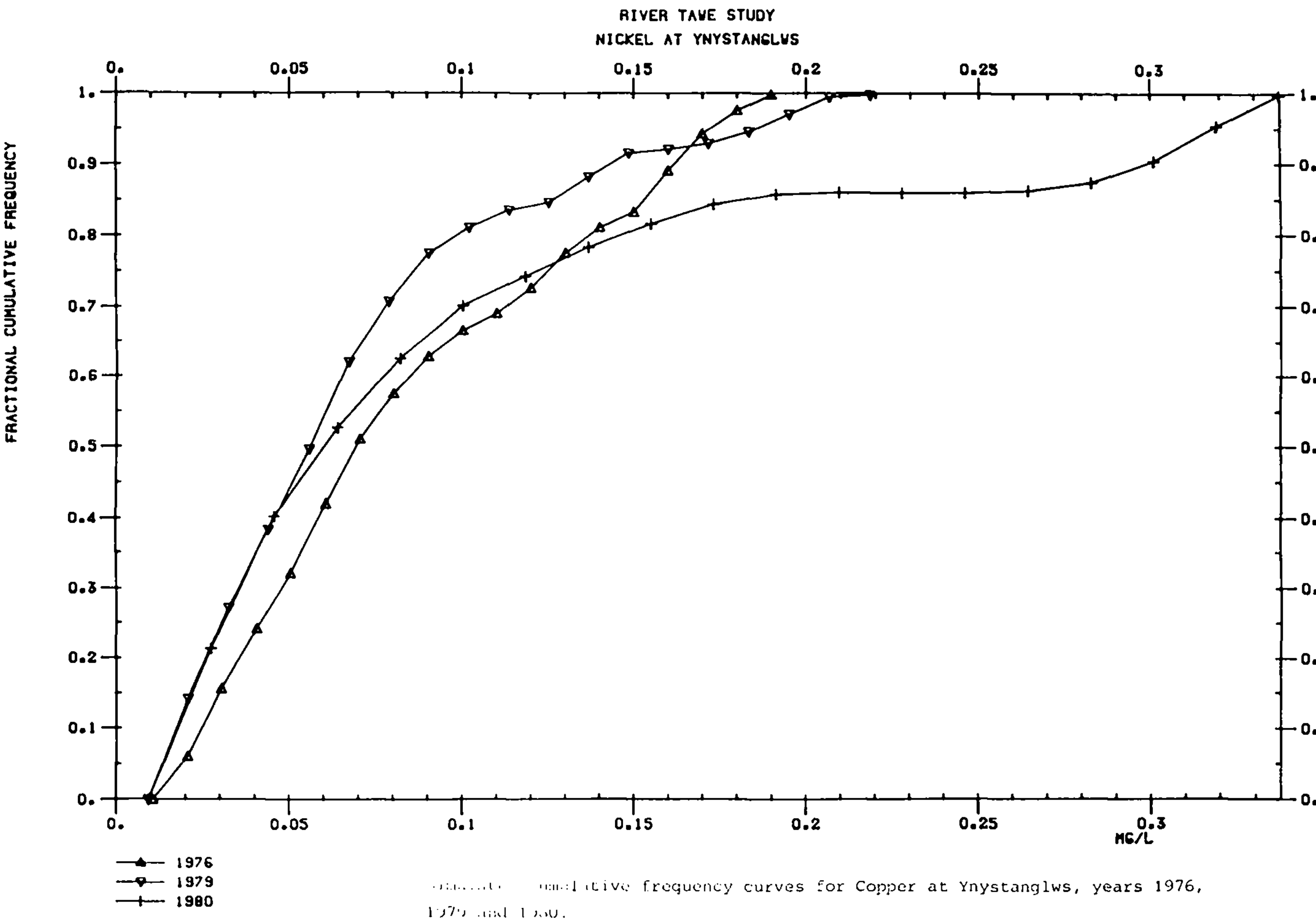


Figure 4.11 Simulated cumulative frequency curves for Copper at Ynystanglws, years 1976, 1979 and 1980.



[illegible] Cumulative frequency curves for Copper at Ynystanglws, years 1976, 1979 and 1980.

The metal bearing tributary, the Nant-y-Fendrod, that enters the Tawe just above Landore primarily affects three of the modelled metals, Manganese, Cadmium and Zinc. These three metals behave differently under the three types of hydrology at Landore than they do at sites where they are affected only by industrial effluents. Thus the 95 percentile value for manganese was highest in the 'average' year of 1980 and lowest in the 'dry' year of 1976 although the 'wet' year of 1979 is only slightly higher. The 95 percentile cadmium value was highest in 1980 with 1979 and 1976 values about the same. The 95 percentile value for zinc is about the same for 1980 and 1976 both these being higher than the 1979 value. The means of these three metals over the three years all follow the sequences of 1980 being greater than 1976 which in turn is greater than 1979.

4.4 The Impact of Sedimentation and Resuspension on River Quality Objectives

To investigate the effects of sedimentation and resuspension on the 95 percentile values the model equations 3.7 have been modified to incorporate sediment exchange. The term S in 3.7 has been defined as

$$S = - K C_2 S_0(+) + (1-K) C_3 u$$

where

$$\begin{cases} 1 \text{ for } u \leq C_1 \\ 0 \text{ for } u > C_1 \end{cases}$$

Here $S_0(t)$ is the upstream sediment concentration, C_1 is a threshold velocity below which sedimentation occurs at a rate C_2 and C_2 is a resuspension parameter which when multiplied by the velocity, u, describes the rate of resuspension.

Model Sensitivity

The sensitivity of the model to the three parameters C_1, C_2 and C_3 was investigated by running the model with various combinations of values for the three parameters. For each set of parameter values the model was run for one year using three data sets selected to represent different hydrological conditions. The years chosen were 1976, 1979 and 1980 selected to represent 'dry', 'wet' and 'average' years respectively. The results, which are summarized in terms of mean and 95-percentile concentrations, are given in Tables 4.1, 4.2 and 4.3.

The values for the means and 95-percentile vary as would be expected. For example for fixed values of the resuspension rate and sedimentation rate the mean and 95-percentile values decrease with increasing critical velocity. This is the case for all the three years investigated. The sensitivity of the model to changes in the critical velocity is low with a four fold change in the critical velocity producing a maximum change in the mean concentration of suspended sediments of 18% in the 'wet' year of 1979. This relatively low sensitivity is reflected in the remaining sets of results with the largest percentage change in 95-percentile concentration occurring in 1980 when increasing the resuspension rate for fixed values of sedimentation rate and critical velocity, caused only a 23% increase.

To investigate the sensitivity of the sediment effects on heavy metal concentrations, the chemical model for total iron was modified as follows:

$$\frac{dI_o(t)}{dt} = \frac{Q_i(t)}{V} I_i(t) - \frac{Q_o(t)}{V} I_o(t) + \frac{Q_T(t)}{V} I_T(t) + \frac{Q_e(t)}{V} I_e(t)$$

$$- K\, C_2 C_4 S_o(t) + (1-K)\, C_3 C_4 u$$

$$K = \begin{cases} 1 \text{ for } u < C_1 \\ 0 \text{ for } u \quad C_1 \end{cases}$$

where I is the total iron concentration (mg/ℓ)

C_4 is the iron content of the suspended sediments (mg/mg)

Table 4.4 Effect of Critical Velocity (C_1) on Total Iron concentration for fixed Resuspension rate (C_3) and Sedimentation rate (C_2). rate (C_2).
$C_2 = 0.5$ day^{-1}, $C_3 = 5.0$ mg/m

	1976		1979		1980	
C_1 m/s	Mean	95%	Mean	95%	Mean	95%
0.25	0.504	1.123	0.465	1.009	0.569	1.413
0.5	0.493	1.091	0.449	0.923	0.552	1.394
1.0	0.478	1.038	0.455	0.988	0.560	1.429

Table 4.5 Effect of Resuspension rate (C_3) on Total Iron concentration for fixed Critical Velocity (C_1) and Sedimentation rate (C_2).
$C_1 = 0.5$ m/s, $C_2 = 0.5$ day^{-1}.

	1976		1979		1980	
C_3	Mean	95%	Mean	95%	Mean	95%
5.0	0.493	1.091	0.449	0.923	0.552	1.394
10.0	0.489	1.050	0.468	0.964	0.562	1.587
20.0	0.492	1.069	0.464	0.910	0.573	1.403

Table 4.6 Effect of Sedimentation rate (C_2) on Total Iron concentration for fixed Critical Velocity (C_1) and Resuspension rate (C_3)
$C_3 = 5.0$ mg/m, $C_1 = 0.5$ m/s

	1976		1979		1980	
C_2	Mean	95%	Mean	95%	Mean	95%
0.1	0.506	1.049	0.477	1.016	0.555	1.417
0.5	0.493	1.091	0.449	0.923	0.552	1.394

The iron content of the suspended sediments was evaluated by regressing particulate iron concentration against suspended sediment concentration, S, measured during a storm event at Ynystanglws and Landore. The resultant relationships were as follows:

Ynystanglws: $I^T = 2.0 + 0.0233S$ $R^2 = 96.4\%$
Landore: $I^T = 0.0 + 0.0220S$ $R^2 = 95.0\%$

where I^T is the total iron concentration (mg/ℓ)
S is the suspended sediment concentration (mg/ℓ)

Using this information an average value for the parameter, C_4, was taken to be 0.023 mg/mg for the entire modelled section of the River Tawe.

Model Sensitivity

To test the sensitivity of this model to the parameters C_1, C_2 and C_3 the same procedure was followed as for the suspended sediment model. In this case the variability of the mean and 95 percentile concentration was even less than for the suspended sediments. Tables 4.4, 4.5 and 4.6 show that no set of parameters cause variations of more than about 5% except in the wet year of 1979. In this year the effect of increasing the sedimentation rate (C_2) is to decrease the 95 percentile and mean concentrations by 6 and 10% respectively. Whilst these decreases are not excessive they will have an effect on setting of effluent standards. If the sediment effects were taken into account in the setting of standards, the effluent concentration could be increased by 10% to meet the required mean river quality objective. Of course this would imply an additional build up of metals in the sediments which might be detrimental to aquatic flora and fauna. It appears therefore that sediment effects are important in assessing the impact of effluents on river systems.

4.5 The Effects of Bank-Side Storage Control on 95% Percentiles

The usual idea of bank-side storage of effluent is that the storage period will allow some further purification of the effluent. This maybe as a result of sedimentation of particulate material or the removal of chemical species by biological action. In the present study a bank-side storage scheme was proposed for the effluent discharged from the Inco Nickel works into the River Tawe just upstream of the gauging station at Ynystanglws.

The idea behind this bank-side storage plan was not to perform any further purification of the effluent but to use it to control the concentration of nickel in the main river. This would be done by storing the effluent in the tank and determining the amount released into the river according to the river flowrate. The idea being that with a large enough tank the effluent flowrate could be kept at a fixed proportion of the river flowrate.

The River Tawe model was used to investigate the effect of bank-side storage on the nickel concentration in the River Tawe. Further, the effect of different sizes of tank, different effluent flowrates and different hydrological conditions were all investigated.

Figure 4.10 shows the effect of changing the effluent flowrate and the bank volume on the 95-percentile nickel concentration in the River Tawe at Ynystanglws. The most obvious feature is the very sharp fall in the 95-percentile value at a given bank volume. This is true whatever the effluent flowrate. The bank volume that gives the sudden fall in the 95-percentile value can be called the optimum tank volume. The optimum tank volume probably represents the volume required to contain the excess of effluent flow rate over allowed effluent flowrates during the low flow summer period.

Figure 4.11 shows the effect on the bank volume and 95-percentile concentration caused by different hydrological conditions acting on the same effluent flowrate. Again there is the clearly defined optimum bank volume for each year which vary considerably from year to year. 1980 is the year which requires the largest tank which is probably due to the long low flow period that prevailed during the early summer of that year. The smallest tank would have been required in 1979 which was the wettest year of the three.

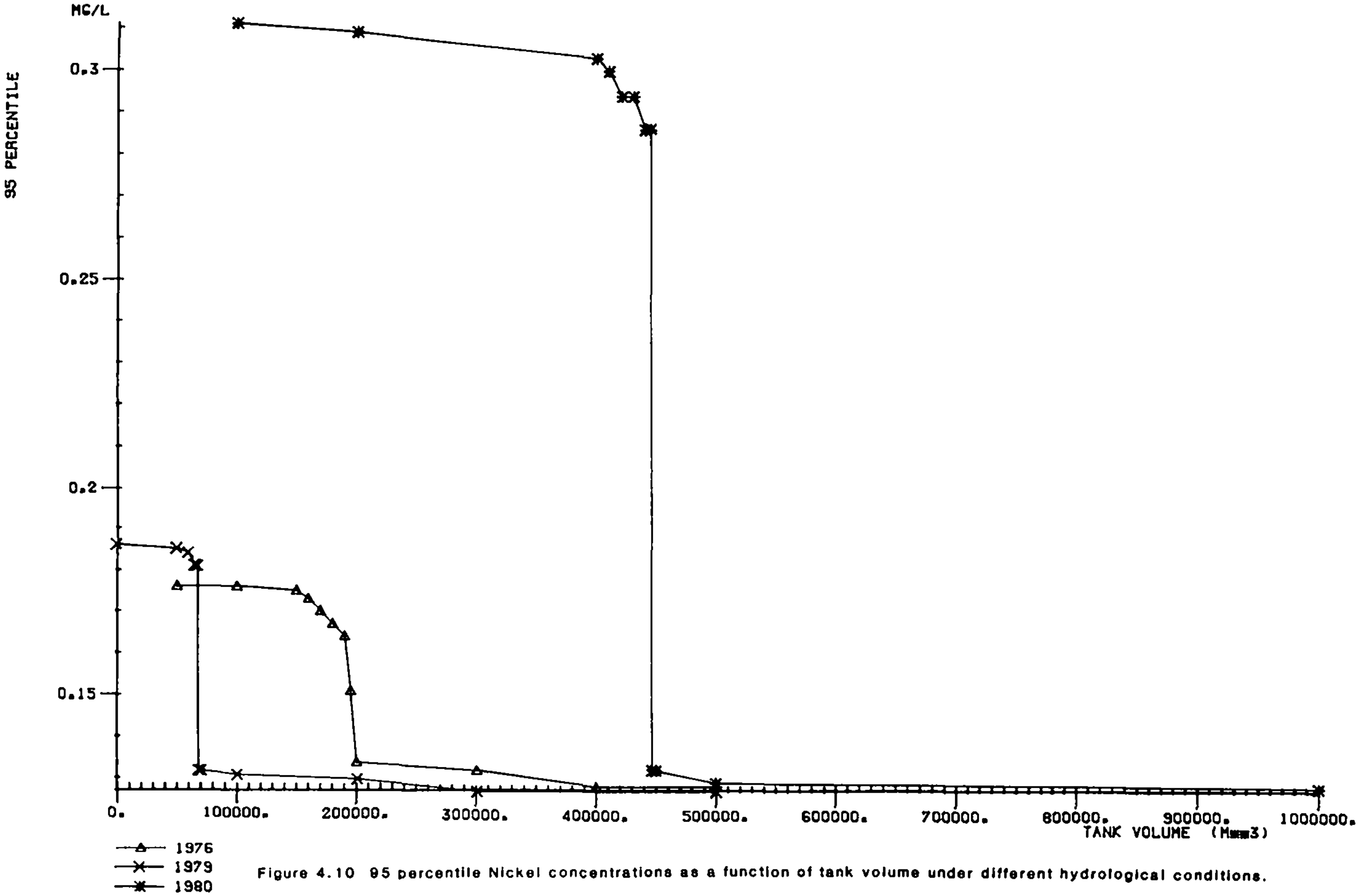


Figure 4.10 95 percentile Nickel concentrations as a function of tank volume under different hydrological conditions.

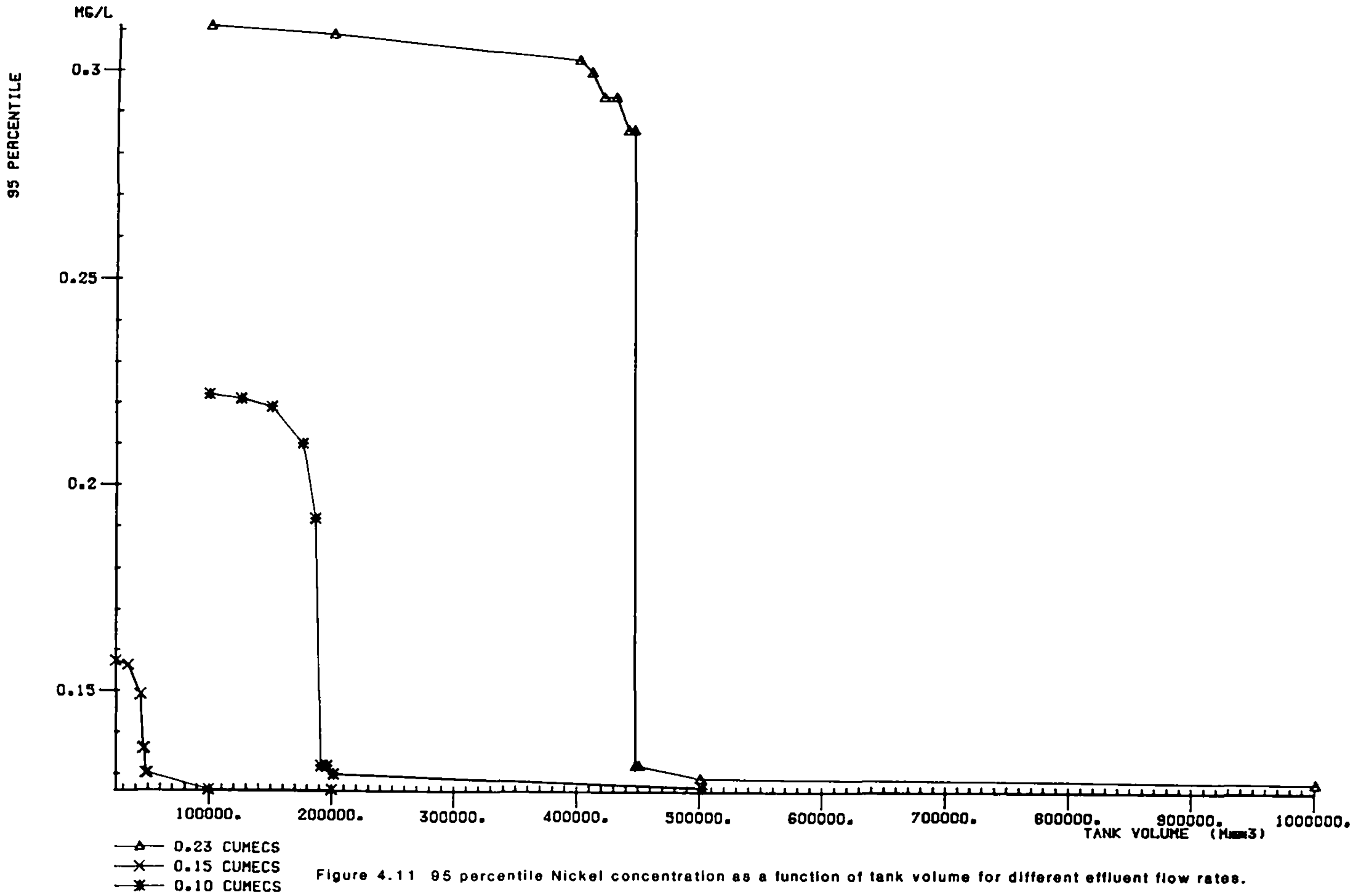


Figure 4.11 95 percentile Nickel concentration as a function of tank volume for different effluent flow rates.

It should be noted that these results indicate how difficult it would be to design a tank of the correct volume for a given effluent that would be appropriate for every year. Too big a tank would waste money since it might only be needed once or twice in its life, whereas too small a tank may not be of any benefit to the river whatsoever. It maybe possible to carry out further research into the relationship between hydrological 'low flow' statistics and the optimum tank volume for a given river but this report can do no more than point others in that direction.

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SECTION 4 - IDENTIFYING POLLUTANT SOURCES USING DISPERSION THEORY

ON THE IDENTIFICATION OF POLLUTANT OR TRACER SOURCES USING DISPERSION THEORY

by

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ABSTRACT

A technique has been investigated for the identification of the source of a pollutant or tracer entering a river system. The approach is based on dispersion theory and uses an optimization algorithm to estimate Peclet numbers and dispersion coefficients from tracer experiments conducted over a range of flow rates prior to application to pollution problems. Data from the Bedford Ouse River in South-Eastern England and White Oak Run in Virginia U.S.A. are used to demonstrate the approach. The variation of stream velocity and dispersion coefficient with flow rate is investigated. The sensitivity of the technique to errors in the dispersion coefficient is evaluated. It is concluded that experimentally derived dispersion coefficients are preferable to values obtained using hydraulic or channel geometric approaches.

KEY WORDS

Pollution, Dispersion Theory, Tracer Experiments, Rivers, Peclet Numbers, Locating Polluting Sources, Optimization, Dispersion Coefficient.

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INTRODUCTION

A common problem in the area of water pollution control is the identification of an unknown pollutant source along a given river and the prediction of dispersion characteristics. Pollutants are often detected at a monitoring station on a river from such measurements as conductivity, ammonia or dissolved oxygen levels (Whitehead et al, 1984) or may be investigated during field experiments (Brady and Johnson, 1981). Water protection agencies must react quickly to the pollution incident by monitoring the pollution as it moves downstream, determining travel times, and warning abstractors of the extent and duration of the pollution. In these situations it is desirable to identify the source of the pollutant so that the exact nature of the pollutant is determined and the discharge curtailed or stopped. In certain cases the source of the pollutant can be identified from its chemical constituents. For example in the case of a trace toxic chemical there may be only one manufacturer along the river system and identification is straightforward. However, in the case of discharge of biodegradable organic matter or ammonia there may be several candidate sources such as sewage overflows, the breakdown of activated sludge treatment processes, discharges from industry and field runoff. Identifying the pollutant source under these conditions can be a difficult procedure. The object of this paper is to develop an approach to the solution of this problem based on dispersion theory and to investigate the sensitivity of this technique to errors in the dispersion coefficient. The technique is also applied to tracer experiment data to estimate velocities, dispersion coefficients and Peclet numbers in order to characterise stream behaviour.

THEORY

Pollutants entering river systems are subject to dispersion processes which redistribute the polluting material within the river. In a pioneering study of dispersion, Taylor (1954) asserted that the primary dispersive mechanism in shear flows is the variation in convective velocity within the cross-section and showed that, in this case, the process could be described by a one-dimensional Fickian diffusion equation,

$$\frac{\partial c}{\partial t} = - v \frac{\partial c}{\partial x} + D \frac{\partial^2 c}{\partial x^2} \qquad (1)$$

in which c is the cross sectional mean concentration, v is the cross sectional velocity, t is time, x is distance in direction of flow and D is the dispersion coefficient. Although Taylor's theory of longitudinal dispersion applied to rivers has been criticized (Thackston and Krenkel, 1967, Fischer, 1981), the theory, along with embellishments, remains the most widely used technique among practioners. Consequently, although other models are available that may avoid the criticisms of Taylor's theory as applied to natural rivers (e.g., Beer and Young, 1983, Whitehead et al. 1979, 1981), the convection diffusion equation is retained in this study so that results can be discussed in terms of the widely-accepted dispersion coefficient.

A modification of equation (1) that accounts for losses (decay, adsorption on sediments, etc.) has been chosen for this study. Equation (1) can be modified to account for these losses and to allow for the addition of effluent into the river as follows.

$$\frac{\partial c}{\partial t} = - v \frac{c}{x} + D\frac{\partial c^2}{\partial x^2} + q(c_i - c) + K \qquad (2)$$

where q is the rate of discharge per unit length of the river, c_i is effluent concentration, K is the reaction rate. K can be of the following form:

$$K = \mu - \lambda c - \alpha\frac{\partial c}{\partial t} \qquad (3)$$

where μ represents the generation of a substance due to a chemical reaction or, if negative, a loss due to the constant irreversible adsoption on the river sediments; $- \lambda c$, represents reactions proportional to concentration such as biodegradation; and the third term represents those reactions proportional to a temporal change in concentration.

De Smedt (1981) has given a solution to equation (2) subject to the boundary conditions.

$$c_1(t) \text{ at } x = 0,$$

and $\frac{\partial c}{\partial t} = 0$ as $x \rightarrow \infty$

The downstream concentration $c_2(t)$ can be written as

$$c_2(t) = c_o + \int_{-\infty}^{t} \frac{\sqrt{P_e}\, c_1(t-\tau)}{\sqrt{4\pi\, \tau/t_o}} \exp\left[\frac{P_e(1 - \tau/t_o)^2}{- 4\, \tau/t_o} - (1-F)\frac{\tau}{t_o}\right] \frac{d\tau}{\tau} \qquad (4)$$

Four parameters appear in this equation:

(1) the average transport time t_o, given by

$$t_o = \frac{L(1 + \alpha)}{v} ; \qquad (5)$$

where L is the reach length

(2) a loss factor F, given by

$$F = 1 - \frac{(q + \lambda)L}{v} \qquad (6)$$

(3) the base or background concentration, c_o, given by

$$c_o = \frac{q\ c_i + \mu}{q + \lambda}\ [1 - \exp\ (\frac{x\ (v-u)}{2D})\ ]; \qquad (7)$$

where

$$\sqrt{v^2 + 4(q + \lambda)D} ;$$

(4) the Peclet number P_e, given by

$$P_e = \frac{vL}{D} \qquad (8)$$

These four parameters can be estimated using an optimization routine applied to upstream and downstream water quality data. De Smedt ~~et al.~~ (1981) have applied this technique to data obtained for the Albert and Campinean canal network of Northern Belgium. In this paper we describe the application of this optimization procedure to three problems; firstly the direct determination of travel time and dispersion coefficients using tracer experiment data; secondly the variation of velocity and dispersion coefficients with flow: and thirdly, the identification of the source of a pollution given concentration data over a pollution event.

In this third application it is assumed that the stream velocity and the dispersion coefficient are known from tracer experiments over a range of flow rates or have been estimated from hydraulic and channel properties. Since the distance upstream to the pollution source, L. is not known it is necessary to guess this initially and employ an iterative procedure in which P_e is calculated using equation (8) and fixed, and the other three parameters are estimated using the opitmization algorithm. This results in a new value of t_o which is used to calculate L from equation (5), assuming α is zero. Assuming α is zero is not an unreasonable assumption for most non-conservative determinands, since the loss processes will generally have reactions proportional to concentrations rather than to the temporal change in concentration. Using the new value of L, P_e is recalculated and the optimization repeated. This iterative procedure converges rapidly to give a stable value of t_o and hence L. The convergence is achieved because L, t_o and hence P_e control the shape of the concentration curve at the downstream site and there is a unique solution to this fitting problem. However the solution is sensitive to errors in the velocity or dispersion coefficient and we investigate this sensitivity later in the paper.

APPLICATION TO CONVERVATIVE TRACERS OR POLLUTANTS

We now illustrate the applications described above using data on the movement of conservative tracers in the Bedford Ouse River. First the dispersion coefficient and velocity are estimated from a series of tracer experiments conducted over a range of flow rates. Relationships between velocity dispersion coefficient and flows are determined and then the iterative procedure outlined above is implemented to determine the location of the tracer input. Finally, the sensitivity of the estimated t_o to values of the velocity and dispersion coefficient is examined.

In order to evaluate velocity, flow and dispersion characteristics on the Bedford Ouse a series of tracer experiments has been conducted by personnel of the Institute of Hydrology (IH) in collaboration with the Anglian Water Authority. A known mass of sodium iodide (NaI) dissolved in water was added to the river as an impulse input. At a downstream site a selective ion electrode was used to monitor the iodide concentration continuously and water samples taken at appropriate intervals for chemical analysis in the IH laboratory. Experiments were conducted on five separate occasions. A typical concentration curve for the Bedford Ouse is given in Figure 1. Table 1 indicates the range of flows over which the five experiments have been conducted. Iodide can be treated as conservative since, although Neal and Truesdale (1976) have shown that it is adsorbed onto organic sediment, organic sediment levels are low in the Bedford Ouse. For each tracer experiment the dispersion equation model and optimization techniques have been applied to estimate t_o and P_e from the observed concentration curve.

The optimization results for all five tracer curves are presented in Table 2 together with statistics relating to the % variance explained by the model. In every case a good fit is obtained, although in certain cases (see Figures 2,3,4,5 and 6) the trailing edge of the model output is below the observed tracer curve. This is to be expected given that

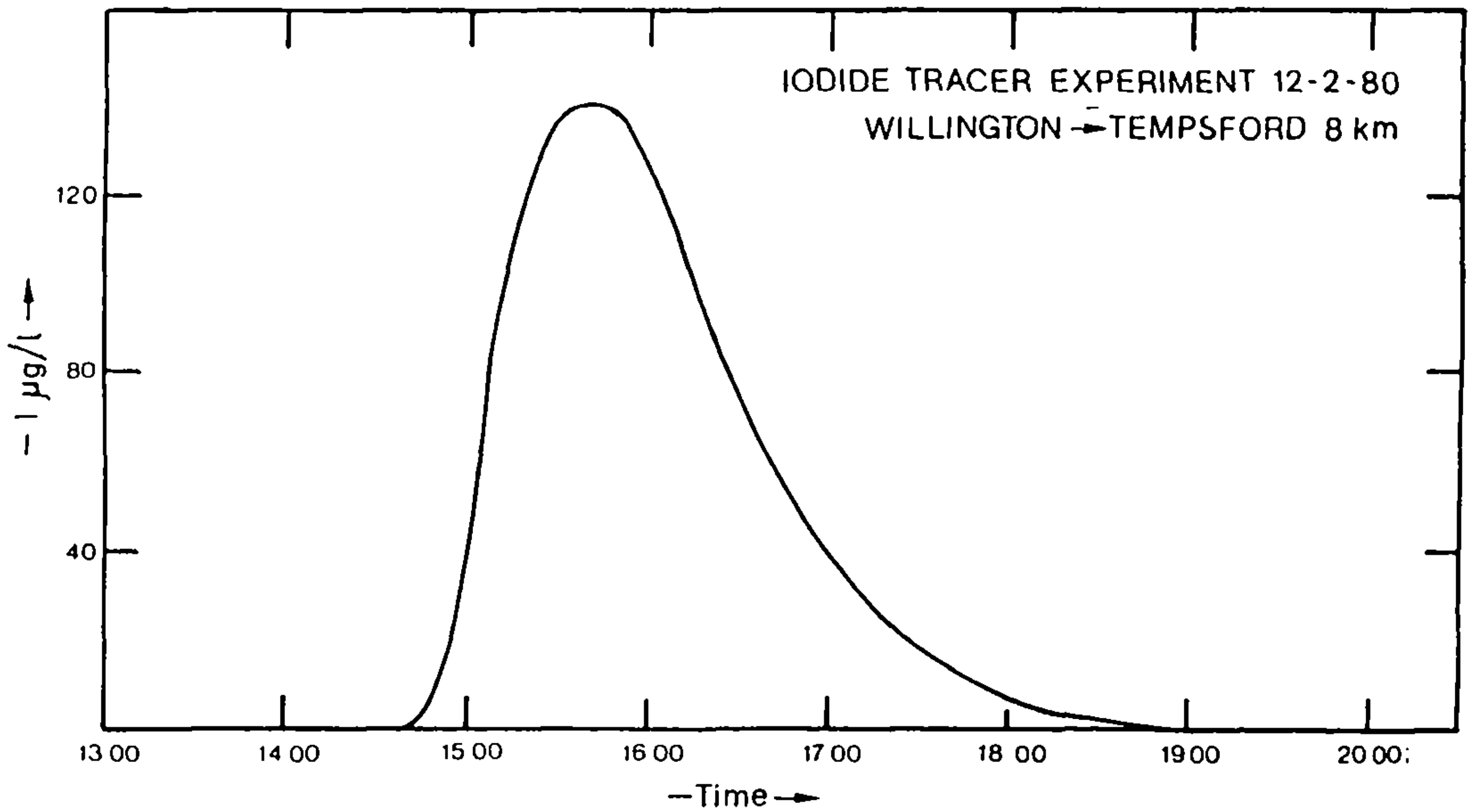

Figure 1. Iodide Tracer Experiment on the Bedford Ouse

Table 1 Tracer Experiments on the Bedford Ouse

Flow rate $m^3 s^{-1}$	Time to First Arrival Hours	Time to Peak Hours	Distance kms
2.0	64.0	74.0	19
6.8	11.0	13.6	8
11.5	7.5	10.0	8
27.0	4.3	5.4	8
32.0	4.2	5.1	8

the convection-diffusion model does not include the effect of dead zones and variable channel geometry. Nevertheless the fit appears satisfactory and in each case the optimization routine converged rapidly to the minimum residual error. A typical error surface for the optimization is shown in Figure 7 and indicates the deep valley defining the optimal condition.

The estimated mean travel time, t_o and Peclet number, P_e are given in Table 2 and the mean velocity, v, and dispersion D, are caculated from

$$= \frac{L}{t_o} \qquad (9)$$

and

$$D = \frac{vL}{P_e} \qquad (10)$$

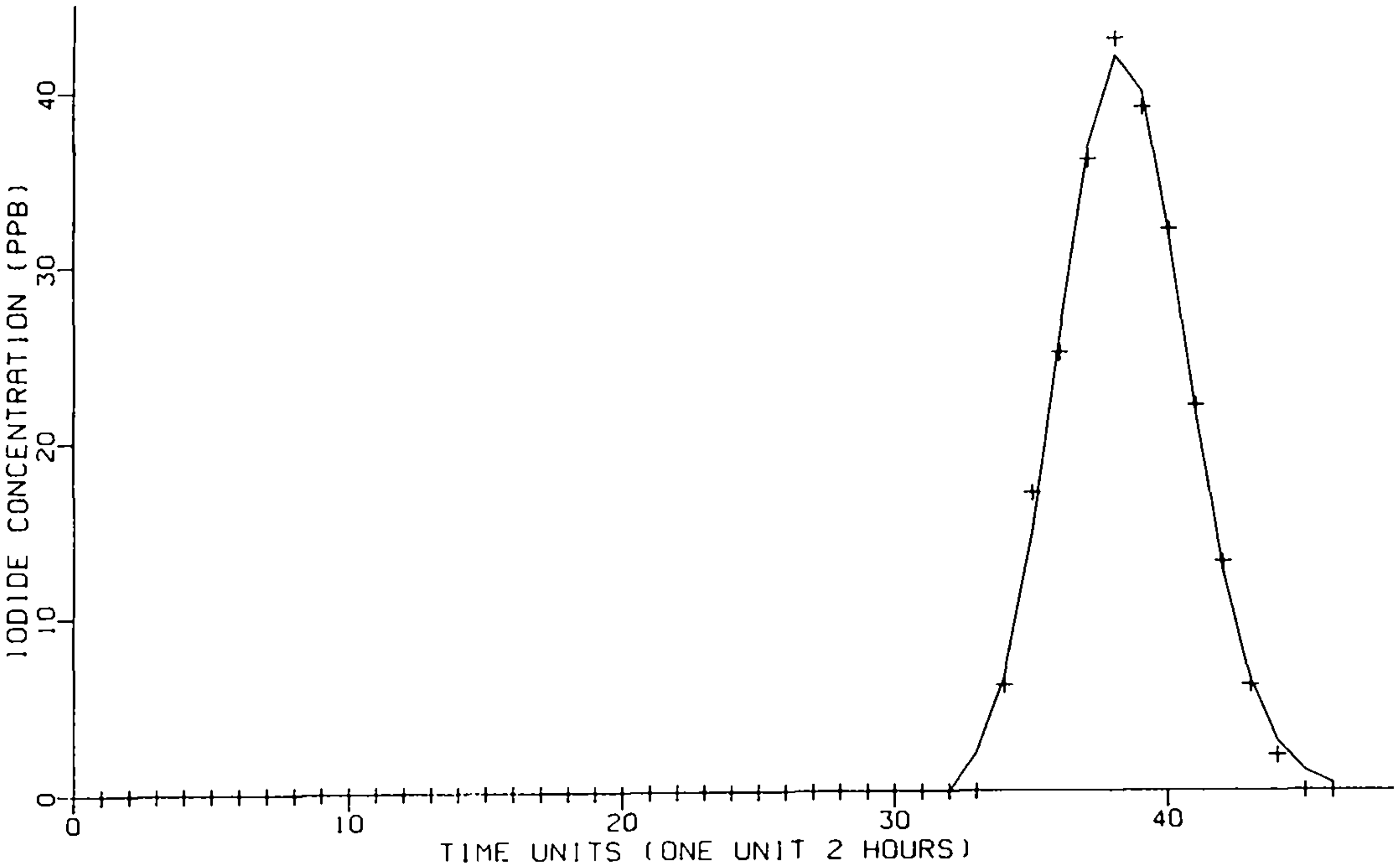

Figure Simulated and Observed Iodide Tracer Results (Flow rate 2 m^3s^{-1})

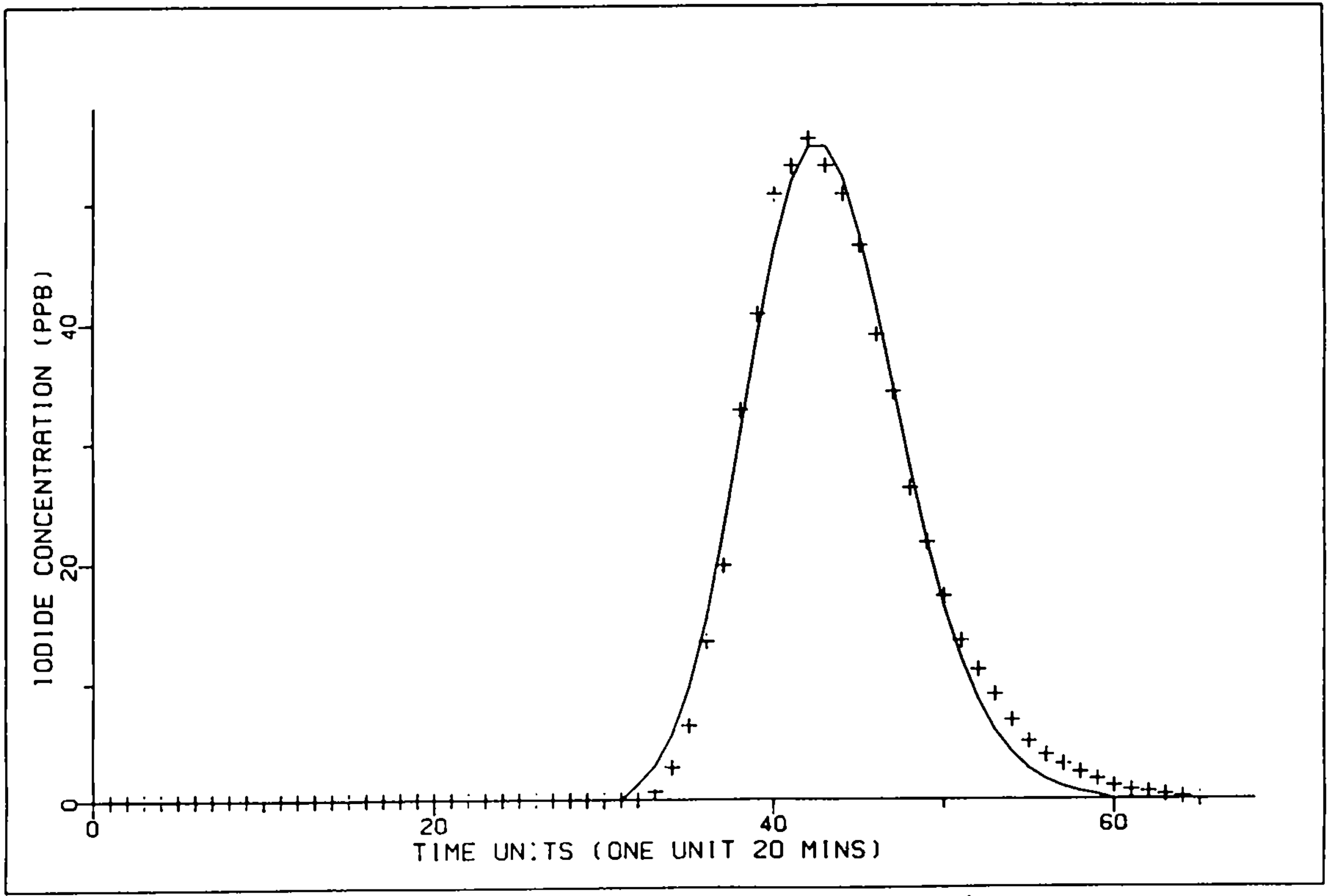

Figure 5. Simulated and Observed Iodide tracer results (Flow rate 6.8 m^3s^{-1})

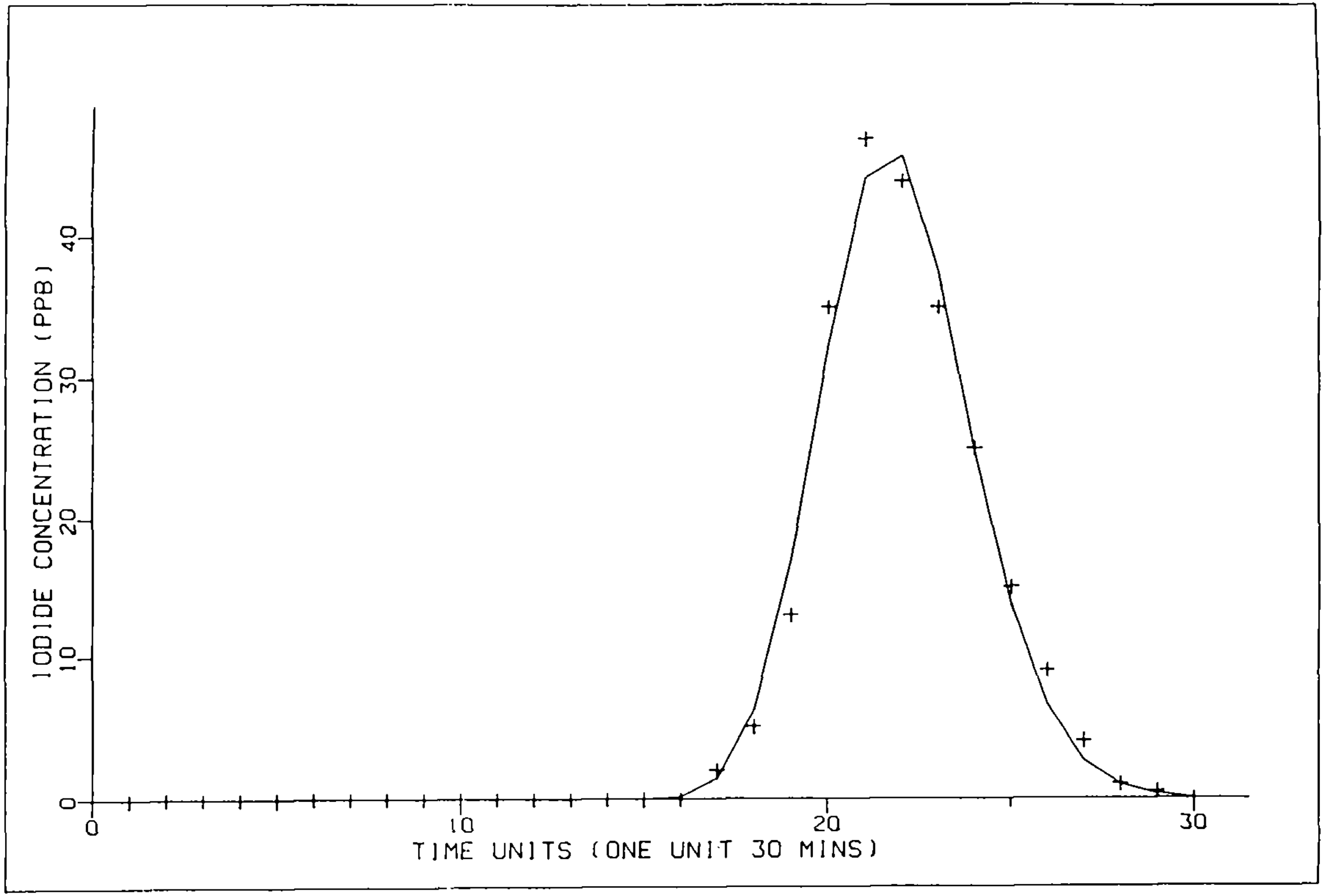

Figure 4. Simulated and Observed Iodide tracer results (Flow rate 11.5 $m^3 s^{-1}$)

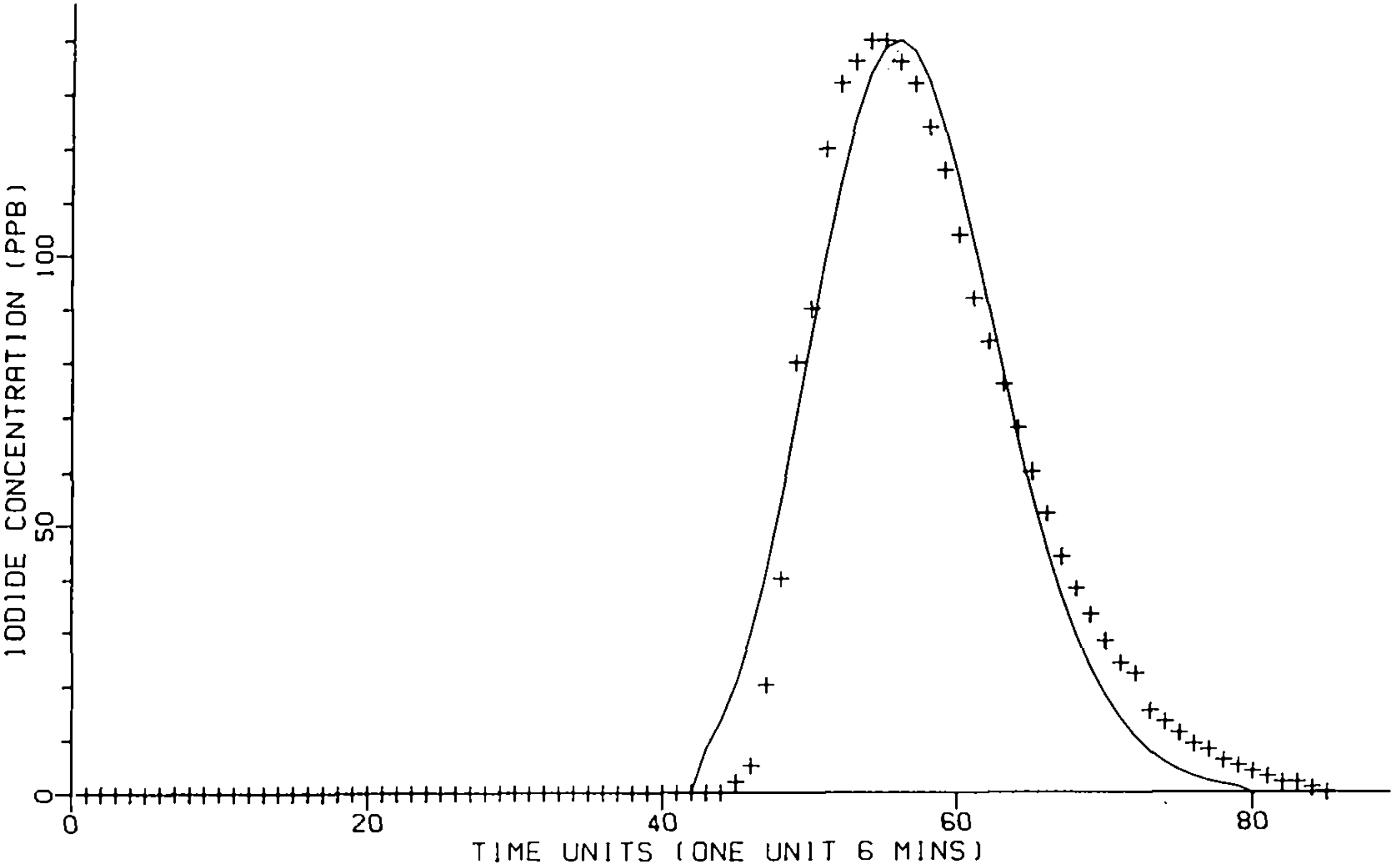

Figure 5. Simulated and Observed Iodide Tracer results (Flow rate 27 m^3 s^{-1})

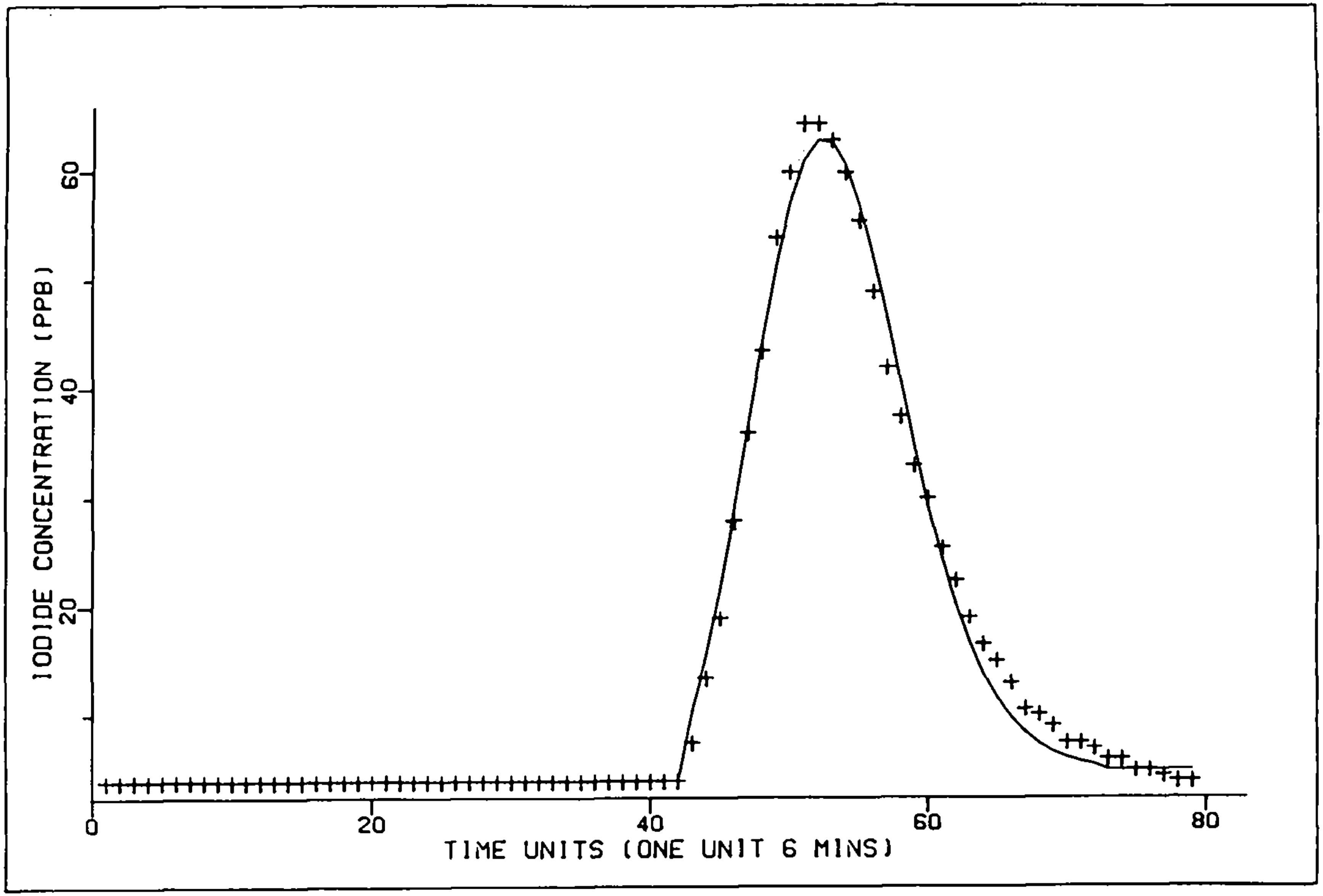

Figure Simulated and Observed Iodide tracer results
(Flow rate 32 $m^{3} s^{-1}$)

Table 2 Optimization results from five tracer experiments

Q $m^3\ s^{-1}$	Estimated t_o Hours	Estimated P_e Dimensionless	v $m\ s^{-1}$	D $m^2\ s^{-1}$	% Variance explained
2.0	73.8	504.6	0.072	2.7	99.5
6.8	14.1	174.7	0.161	7.4	99.1
11.5	10.5	213.5	0.213	8.0	98.7
27.0	5.6	155.7	0.394	20.2	96.0
32.0	5.2	212.8	0.416	15.6	99.3

Since the experiments were conducted over a range of flow conditions it is possible to determine empirical relationships between velocity, flow and dispersion. From a regression analysis of the log transformed variables the following relationships have been derived.

$$= 0.046\ Q^{0.64} \qquad (11)$$

$$D = 1.82\ Q^{0.66} \qquad (12)$$

$$D = 37.7\ v^{1.05} \qquad (13)$$

These relationships characterise the non-linear behaviour of the river system and can be used in any subsequent analysis to identify the source of a pollutant or to model the transportation and dispersion of pollutants.

Consider a hypothetical pollution event in the Bedford Ouse. If we assume that the flow rate is known or can be obtained from gauging records then velocity, v, and dispersion, D, can be determined from equations (11) and (12). From equation (9); $L = t_o v$; substitution of this expression into equation (8) gives an estimate of the Peclet number.

The Peclet number can therefore be determined given an estimate of the mean travel time, t_o. Since the Peclet number controls the ratio of convective processes to dispersive processes, there will be an optimal condition in which the shape of the downstream concentration curve is matched to the model output. However the optimisation is particularly sensitive to errors in the dispersion coefficient, as indicated in Figure 7. As an example of determining the mean travel time, t_o, the iterative procedure is applied to the low flow tracer experiment shown in Figure 2, giving the opitmization routine just the bellshaped concentration curve and an initial guess of L and hence t_o. The iterative procedure was used to update the Peclet number and re-estimate t_o and the final converged value for t_o was found to be 74 hours. Given the velocity, v, of 0.072 m s^{-1} and $L = ut_o$ gives an estimated source location 19.180 kms upstream of the downstream observation site. An error of 180 m in this distance of 19.18 kms was obtained from the estimation procedure which represents less than 1%. For all practical purposes, the estimated distance of 19.18 kms to the pollution input is sufficiently accurate for a water authority to locate a particular discharge.

APPLICATION TO NON-CONSERVATIVE TRACERS OR POLLUTANTS

The experiment on the Bedford Ouse used a conservative tracer and is not necessarily representative of pollution events. In many cases pollutants undergo some form of change on entering a river system. For example, a discharge of ammonia would be subject to nitrification processes or a discharge of heavy metals would be adsorbed onto sediments. In order to illustrate the location finding technique for a non-conservative pollutant, data have been obtained from a sodium iodide dye tracer experiment in White Oak Run in the Blue Ridge Mountains of Virginia. NaI is normally considered a conservative tracer but in this case the leaf litter and high organic content of the stream bed resulted in considerable loss of tracer. As in the case of the Bedford Ouse example it is necessary to first derive velocity and dispersion ceofficients and these were obtained by applying the optimization approach to data at two sampling sites. The results of this analysis are presented in Table 3 and Figure 8 shows the simulated and observed downstream concentration curve at the site farthest downstream.

Table 3 Results of Optimization using White Oak Run tracer data.

Reach length m	t_o minutes	P_e	v $m\ s^{-1}$	D $m^2\ s^{-1}$	% variance explained
56.88	90.75	5.34	0.0105	0.107	99.37

If we now assume that the velocity and dispersion coefficient determined from this analysis apply to the stream for the reach from the injection site to site farthest downstream, then it is possible to determine the input location using the iterative procedure described previously. Initially it is assumed that the tracer is conservative and the Peclet number adjusted via equation (8) using v and D from Table 3 and an initial guess for L and hence t_o. From the iterative procedure the estimated t_o was found to be 115 minutes which gives a distance for the discharge of 72.5 m, assuming the velocity in Table 3 applies over the entire length. The actual distance upstream is 76.6 m and the error in determining the source location is therefore 5.3%. This error is reduced further if the tracer is assumed non-conservative, in which case the estimated t_o becomes 120 minutes giving a distance of 75.6 metres and an error of 1.3%. The opitmization surface is shown in Figure 9 and indicates a broad valley enclosing the optimal condition. The improvement obtained when it is assumed that the tracer is non-conservative arises because the shape of the downstream curve is better approximated by the model with decay included. These results indicate that the technique is applicable to non-conservative pollutants.

SENSITIVITY TO ERRORS IN THE DISPERSION COEFFICIENT

In most rivers little information is available on dispersion coefficients. In order to obtain such information it is necessary to conduct tracer experiments, as in the case of the two streams described above, or to estimate dispersion coefficients from hydraulic or channel geometry data. In the latter case, such estimates are likely to be in error and it is important to investigate the sensitivity of the suggested source location method to errors in the dispersion coefficient.

A universally applicable formula for estimating a longitudinal dispersion coefficient in a natural river from hydraulic and morphometric data is not available. Liu (1977) suggested an approach aimed at overcoming large errors in previously proposed formulae. In Liu's approach:

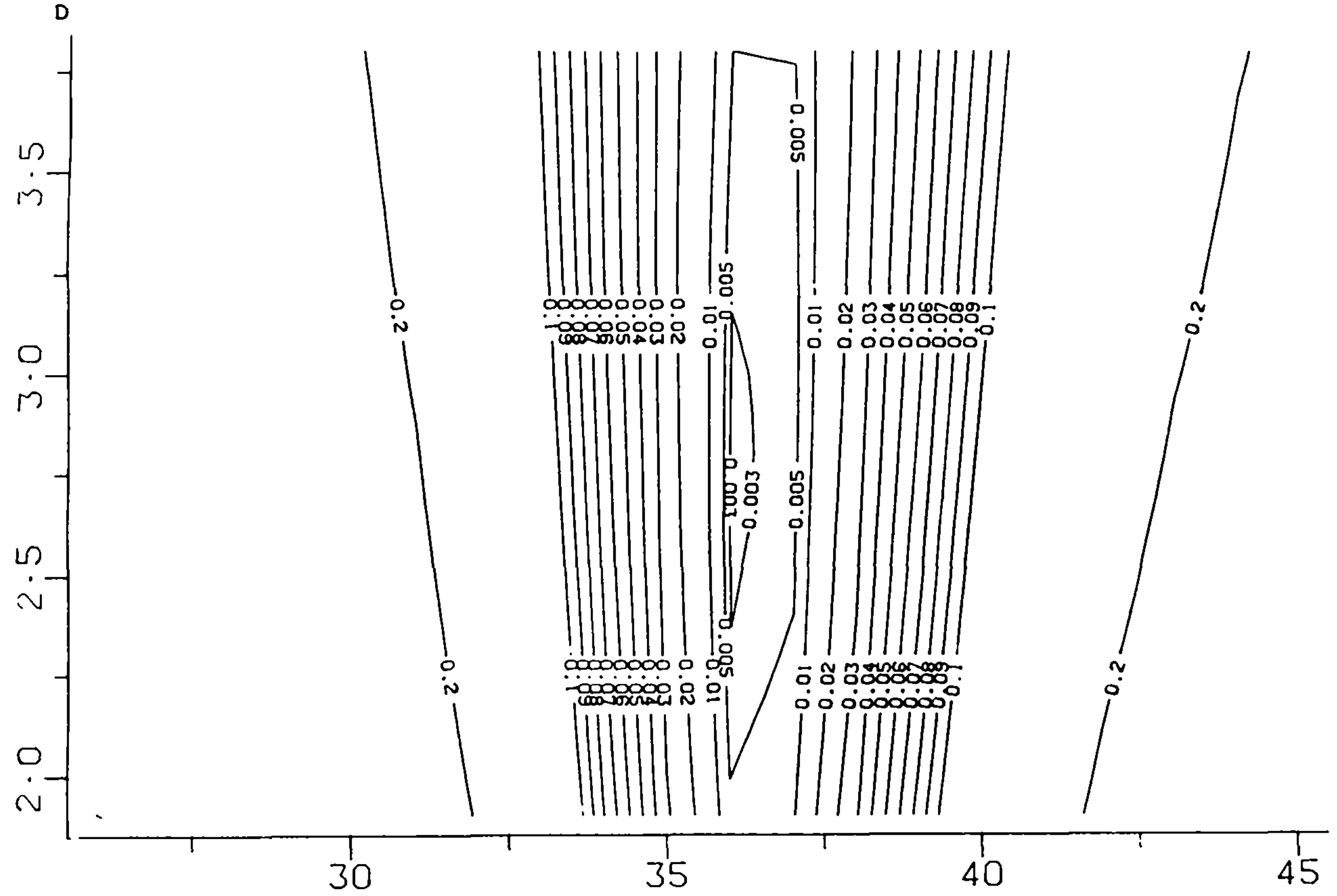

Figure 7. Optimization surface for Bedford Ouse tracer experiment (Flow rate 2 m^3 s^{-1}) based on sum of residual errors squared

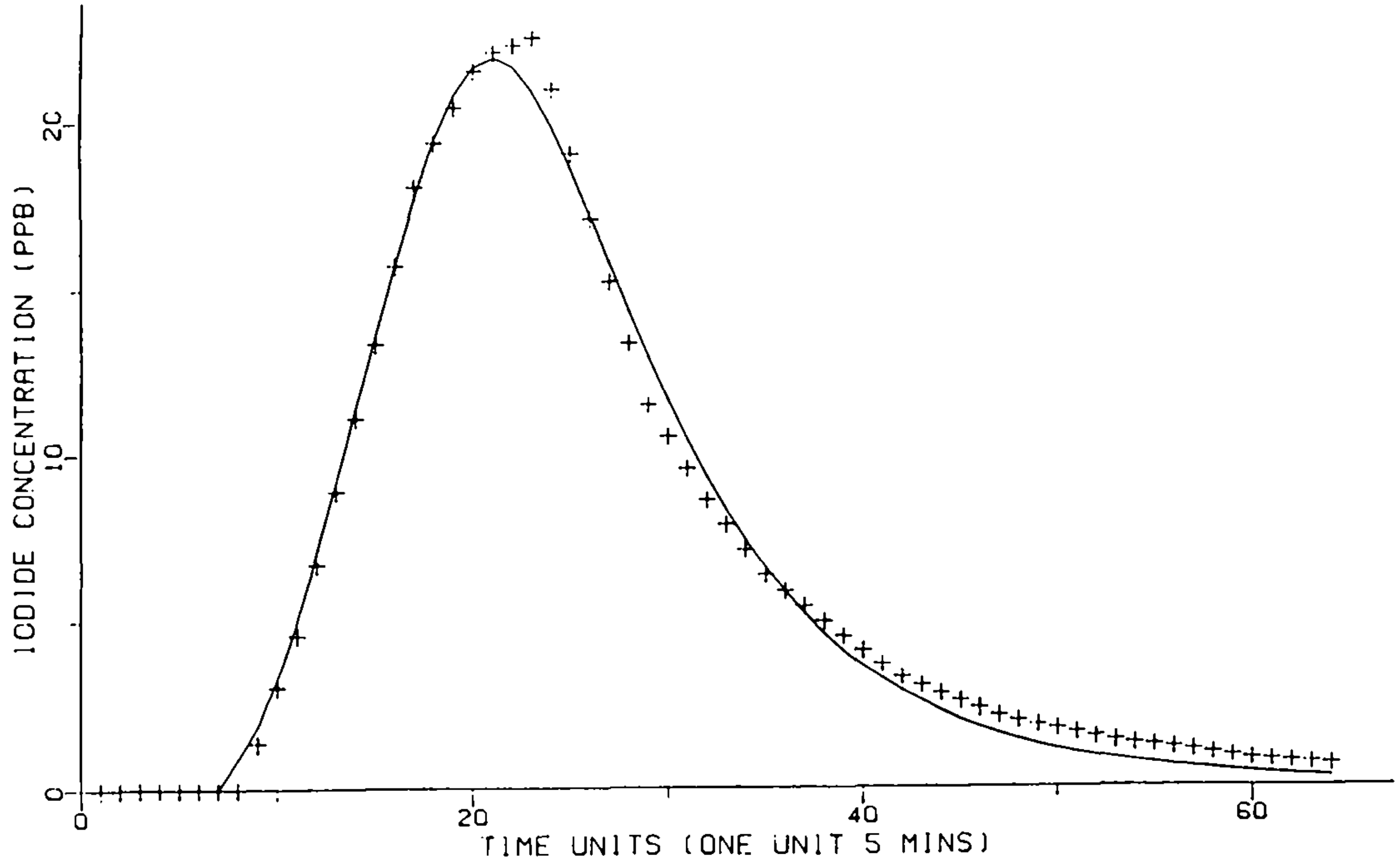

Figure 8. Simulated and Observed Iodide Tracer Results

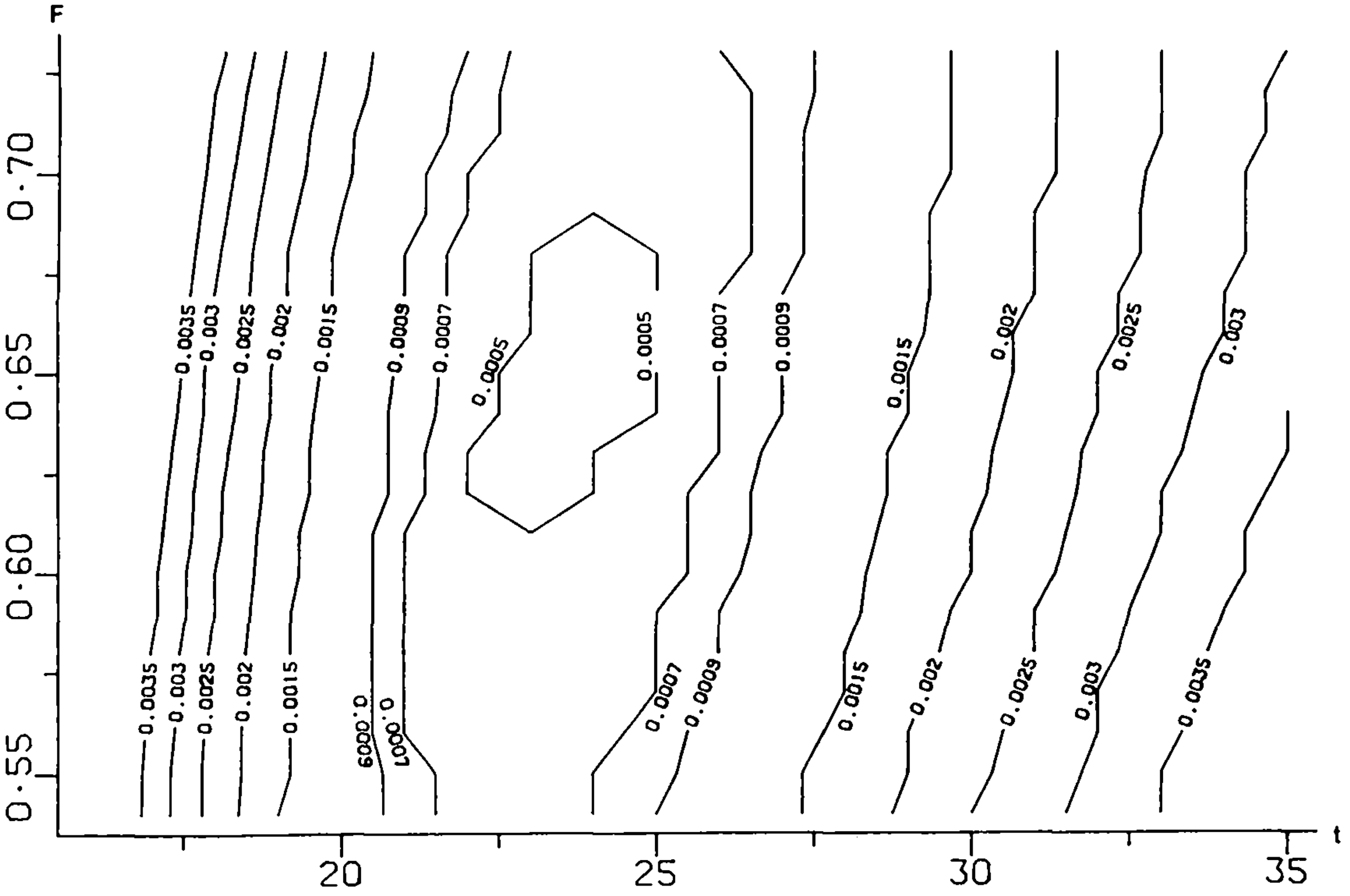

Figure 9. Optimization Surface for White Oak Run data based on sum of residual error squared

$$D = \beta \frac{Q^2}{R^3 U*} \qquad (14)$$

where U* is the friction velocity, ie $U* = (gRS)^{0.5}$; g is the acceleration of gravity; R is hydraulic radius; S is channel slope;

and where β is a channel shape factor given as,

$$\beta = p \left(\frac{U*}{v}\right)^{1.5}. \qquad (15)$$

The coefficient, p, was calculated by Liu to be 0.18, an average value for a number of streams in the USA. He reported that average errors in predicting D from flume experiments was 51% and that, for natural streams, D could be predicted only within a factor of 6.

In order to illustrate the sensitivity of the proposed method for locating a pollution source to errors in the dispersion coefficient, a number of optimization runs were conducted using different values of D in equation (9). The optimal value of t_o increases linearly as D decreases and the mean error in the distance estimated is 75% of the error in the dispersion coefficient. In other words a 100% error in D will result in a 75% error in the source distance. Since the hydraulic or channel geometry methods invariably produce errors of this magnitude it may be inferred that experimental determination of D is preferable to determination by empirical formulae.

CONCLUSIONS

The simulation of pollutants in a river system using dispersion equations is frequently used by researchers and river managers to investigate pollutant movement and redistribution. The more difficult problem of identifying a pollutant source is rarely investigated using dispersion theory. In this paper a technique has been developed which can be used to identify the source of a pollutant or tracer in a river system. The approach uses an iterative procedure to locate sources and provides an accurate estimate given information on the dispersion coefficient and velocity in the stream.

The optimization technique can be applied to tracer data to yield dispersion coefficients and velocity data and a series of tracer experiments in the Bedford Ouse conducted over a range of flow rates have provided equations with which to predict dispersion and velocity at different flow rates. Finally the sensitivity of the source location technique to errors in the dispersion coefficient has been investigated. It is concluded that experimentally derived dispersion coefficients are preferable to the theoretical methods derived using hydraulic or channel geometric approaches.

ACKNOWLEDGEMENTS

The authors are grateful to the Anglian Water Authority for permission to conduct tracer experiments on the Bedford Ouse. The data for White Oak Run were collected as part of a research project funded by the National Park Service under contract CX-0001-9-0038.

NOTATION

= concentration
= dispersion coefficient
= loss factor
g = acceleration of gravity
K = overall reaction coefficient
L = reach length
p = coefficient in channel shape factor
q = effluent discharge rate
Q = river flow rate
R = hydraulic radius
S = channel shape
= time
t_o = average transport time
U^* = average transport time
velocity
distance
μ, λ, α reaction rate coefficients
β channel shape factor

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SECTION 5 - MODELLING THE EFFECTS OF ACIDIC DEPOSITION ON SMALL UPLAND CATCHMENTS

MODELLING STREAM ACIDITY IN U.K. CATCHMENTS

by

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SUMMARY

As part of the joint British-Scandinavian Surface Waters Acidification Programme, the Institute of Hydrology is establishing catchment studies in Scotland and Wales. Data from these catchment studies are being used to develop a range of models for investigating short term and long term changes in catchment acidity. Information on the modelling techniques available at IH is presented together with applications of the models to catchments in Scotland and Wales. They provide examples of how both acidic deposition and conifer afforestation can increase streamwater acidity. Long term trends are predicted. A 50% reduction in current industrial emissions is required to prevent further increase in stream acidity in the Southern Uplands of Scotland.

1. INTRODUCTION

Catchment studies investigating the acidic behaviour of upland streams are expensive, time consuming and difficult to establish due to the complexity of hydrological, chemical and biological interactions. Nevertheless many catchment studies have been and are being established to evaluate short term and long term fluctuations in stream water chemistry. For example as part of the joint Scandinavian - British Surface Water Acidification Programme (Mason and Seip, 1985) major studies are being established in the UK and Scandinavia. Other organisations such as the Welsh Water Authority (Llyn Brianne Study; Stoner et al, 1984) the Solway River Purificatin Board (Loch Dee study; Burns et al, 1982) and the Freshwater Fisheries Laboratory (Loch Ard Study; Harriman et al, 1981) have also established catchment studies following mounting concern over the loss of fisheries in Scotland and Wales and the possible detrimental effects of stream acidity on water resources. Several researchers involved in these studies (Harriman et al, 1981, Gee and Stoner, 1984) have reported elevated acidity and aluminium levels in upland streams draining afforested (conifer) catchments in the UK. Moreover in many of these areas and particularly forested catchments fisheries have deteriorated and restocking programmes have been unsuccessful.

It is with these problems in mind that IH has established a catchment study in Wales at Plynlimon (see Neal et al, 1985). IH is also establishing a catchment study in the Cairngorm region of Scotland in collaboration with DAFS (Department of Agriculture and Fisheries for Scotland), the Macaulay Institute of Soil Science and Imperial College, Department of Civil Engineering. IH is responsible for providing stream gauging, rainfall stations, a weather station, snow surveys, sampling and continuous water quality monitoring. IH is also responsible for the subsequent data management, analysis and interpretation. DAFS is responsible for all chemical and biological analysis, with the exception of snowmelt chemistry, which would be undertaken by IH. The Macaulay Institute is responsible for soil-surveys and soil-water chemistry and Imperial College are establishing plot studies.

The hydrological and chemical data collected from the catchment studies forms the basis of a comprehensive modelling research programme by IH.

Recently there has been considerable use of mathematical models to describe the dominant interactions and processes operating in catchments and to simulate catchment behaviour. Steady state models have been used prescriptively to demonstrate the long term consequences of changes in the industrial emissions of SO_2 (Cosby et al, 1985a, b, Kamari et al 1984). Correspondingly, dynamic models have been successfully applied descriptively to several catchments (Christopherson et al, 1982, 1984). For example, Christophersen et al. have developed a simple conceptual model that reproduces major trends in chemical and hydrological behaviour in Norwegian catchments. This model has been successfully extended (Seip et al, 1985) and applied descriptively to the Harp Lake catchment in Canada. The model has also been applied to two forested catchments in Sweden (Grip et al, 1985).

A wide range of mathematical modelling techniques are available at IH for analysing catchment data. These include CAPTAIN (Computer Aided Package for Time Series Analysis and the Identification of Noisy Systems; Venn and Day, 1977, Whitehead et al., 1986), MIV (Multivariable time series model, Young and Whitehead, 1977), the BIRKENES model (Christophersen et al., 1982), MAGIC (Cosby et al., 1985a), EKF (Extended Kalman Filter, Beck and Young, 1976) TOPMODEL (Beven, 1982) and IHDM (Institute of Hydrology Distributed Model, Morris, 1980).

In this paper several of these techniques are described and applied to investigate short term catchment responses or 'events' and long term acidity of soil and stream waters.

2. TIME SERIES OR 'EVENT' TYPE MODELS

Time series models are suitable where the overall input-putput behaviour is of prime importance and where internal mechanisms are particularly complex. It is assumed that a 'law of large systems' applies (Young, 1978) whereby the combination of all the complex non-linear and distributed elements gives rise to an aggregated system behaviour that is relatively simple in dynamic terms.

Application to Loch Dee

Loch Dee has a remote setting in the Galloway Hills in South West Scotland. The catchment is made up of three sub-basins: Dargall Lane to the west, White Laggan Burn with its tributary the Black Laggan towards the south, and Green Burn entering from the south east. The outflow at the north east end of the loch is the source of the River Dee and up to this itself occupies 1.0 km^2. Catchment altitudes range from 225 m on the loch shore to 716 m on Lamachan at the head of the Dargall Lane. Nearly two thirds of the catchment lies above 305 m (1000 ft). Geologically the area comprises two distinct rock types: Ordovician greywackes/shales and granites of Old Red Sandstone Age (Burns et al., 1982).

In Loch Dee an extensive record of hydrological water quality data has been collected over a five year period (Burns et al., 1982, Langan, 1985). Analysis has been restricted initially to a time series model relating flow to hydrogen ion concentration for the White Laggan sub-catchment. The White Laggan is subject to episodic acidification, primarily attributed to atmospheric inputs (Langan, 1985).

The model fitted is an autoregressive moving average type of the form

$$x_t = - \delta_1 x_{t-1} + \omega_0 u_t$$

where x_t is the hydrogen ion concentration ($\mu eq l^{-1}$) and u_t is the flow ($m^3 sec^{-1}$) in the stream at time t.

The parameters δ_1 and ω_0 were estimated using a time series algorithm applied to 200 **hourly** observations of pH and flow. The parameters were estimated to be;

δ_1 = - 0.680 (standard error 0.012)
ω_0 = 0.659 (standard error 0.022)

and Figure 1 shows the simulated hydrogen concentration against the observed concentration. A remarkably good fit to the data is obtained with 93% of the variance explained and suggests that H^+ion and flow are closely related. However a true test of the model would be to use an additional data set; Langan (1985) has applied the approach to all three subcatchments of Loch Dee and found that equally good models have been obtained for a wide range of storm events. In the case of the White Laggan a mean response time (T) of 2.6 hours is obtained, reflecting the fast response time between output flow and hydrogen ion concentrations.

Further applications of the time series techniques to data from Welsh and Norwegian Catchments are given by Whitehead et al (1986).

3. APPLICATIONS OF THE 'BIRKENES' MODELS

A second class of models have been applied to data from the Loch Dee study. These include the 'Birkenes' model developed by Christophersen et al(1982, 84).

The model comprises of a simple two-reservoir hydrological model operating on a daily timestep upon which has been superimposed the importantchemical processes that control the acidification of catchments. Inputs to the model are precipitation, mean daily temperature, mean daily soil temperature and sulphate deposition rates. Figure 2 shows the principal hydrological and chemical processes operating.

The model outputs daily concentrations of Hydrogen ion, Aluminium,

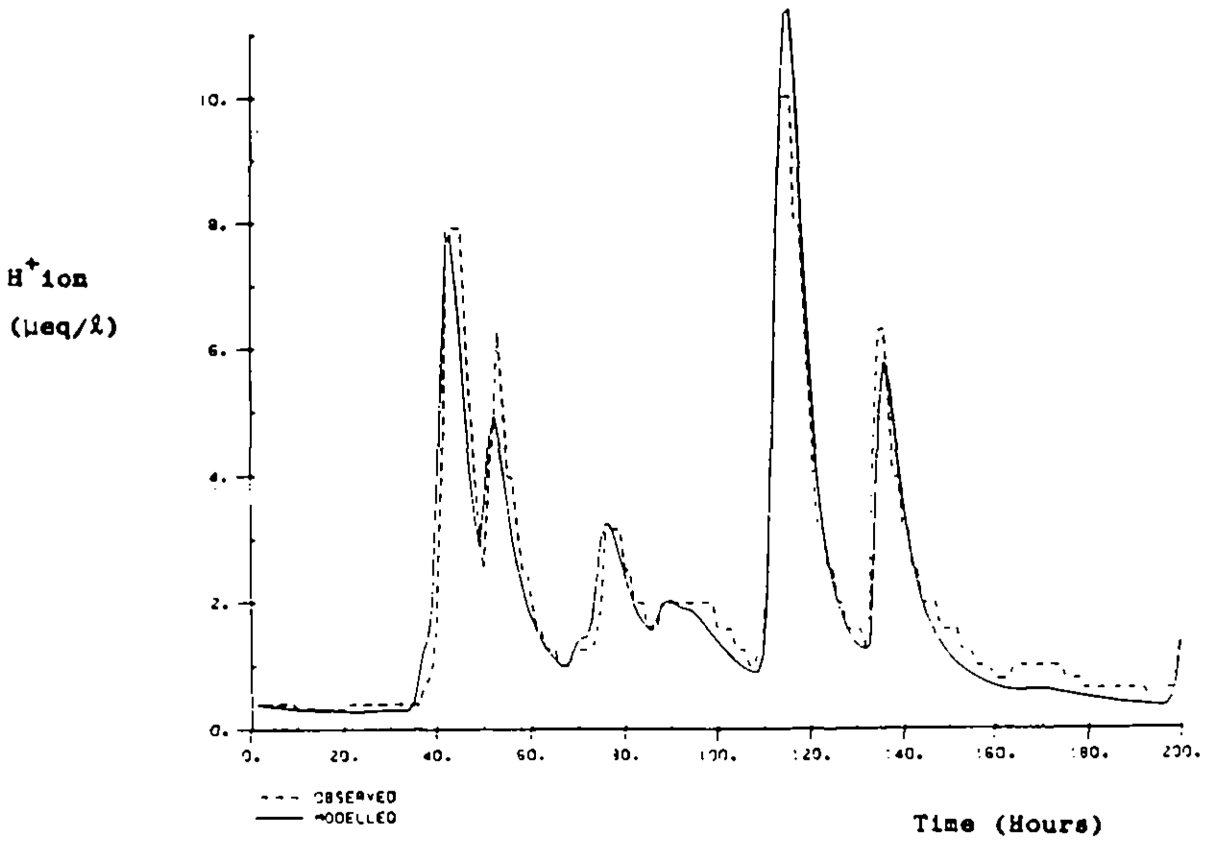
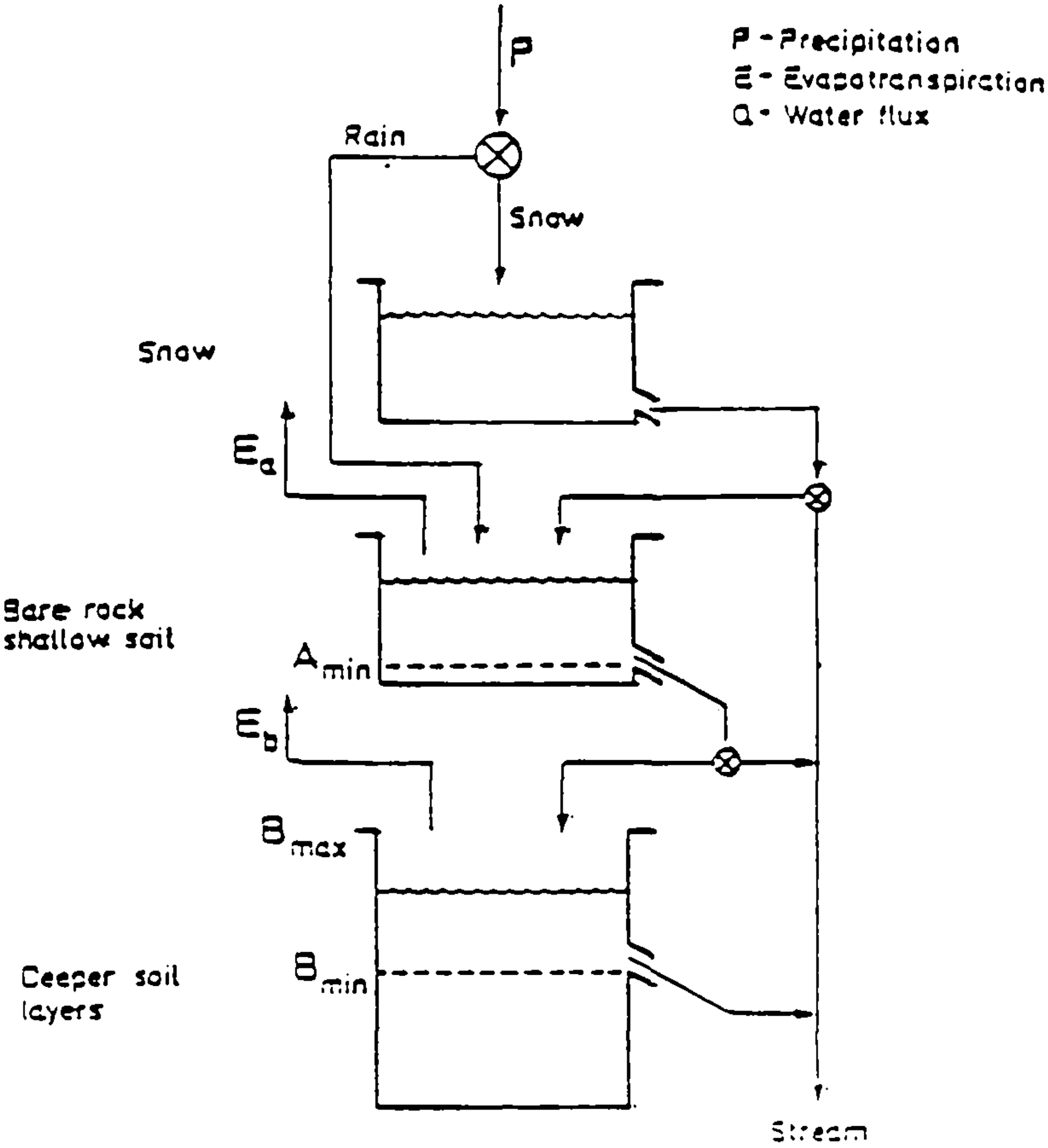


Figure 1

Simulated and Observed H$^+$ ion in the White Laggan, Loch Dee, Scotland, based on the Flow model.



Processes Operating

	Shallow soil reservoir	Deeper Soil Reservoir
H_2O	Precipitation, evapotranspiration infiltration to lower reservoir, discharge to stream	infiltration, evapotranspiration, discharge to stream, piston flow
SO_4	Wet - dry deposition, adsorption/desorption, mineralization	adsorption/desorption, reduction
Ca - Mg	Ion-exchange	release by weathering, adsorption/desorption
H^+	Ion exchange and equilibrium with gibbsite	Consumption by weathering, adsorption/desorption, equilibrium with gibbsite/
Al^{+3}	Equilibrium with gibbsite	Equilibrium with gibbsite, adsorption/desorption
HCO_3^-		Equilibrium with a seasonal varying CO_2 pressure

Figure 2

Hydrological Model used for Harp Lake Catchment and main processes operating

Sulphate, Calcium + Magnesium (M^{2+}) and Bicarbonate in the stream along with predicted flow.

Numerous modifications and additions over the years have resulted in the program structure becoming somewhat confused. Therefore the model has been extensively re-written at IH so as to greatly increase computational efficiency and improve the readability of the FORTRAN 77 source code and hence simplify the task of making modifications in the future.

The ' Birkenes' model has also been used to assess the sensitivity of stream acidity to hydrological parameters and changes in baseflow.

Flow movement between the soil and groundwater compartments is restricted by a "percolation" equation as follows;

$$A_{SIG} = P - (B - B_{min})/B_{max} \qquad \text{for } B > B_{min}$$

and $$A_{SIG} = 1.33P - 0.33P(B/B_{min})^3 \qquad \text{for } B < B_{min}$$

where B refers to the groundwater compartment water level and B_{min} and B_{max} refer to minimum and maximum water levels respectively minimum and maximum water levels respectively (see Figure 2). The parameter, P can be considered as a percolation parameter so that increasing P increases the fraction of flow, A_{SIG}, routed to the lower reservoir. This leads to an increase in the baseflow contribution to the stream. The model also includes a piston flow component to describe the hydraulic movement of water out of the groundwater compartment.

The changes in stream water concentrations for H^+ ion and Al^{3+} to changes in the baseflow contribution to streamwater is highly non linear. This is illustrated in Figures 3 and 4 which show H^+ and Al^{3+} maximums and means over a range of baseflow conditions for both the long and short term data sets: all concentration values fall as the baseflow increases; the rate of decrease varying from one variable to another. In general increases in baseflow results in significant reductions in H^+ ion and Al concentrations. Studies by Seip and Rustad (1983) show a similar non linear behaviour when upper and lower soil horizon waters are mixed.

Further results are given by Whitehead et al (1986) and confirm the sensitivity of the model to parameter, and hence baseflow, changes.

4. APPLICATION OF MAGIC TO LOCH DEE

MAGIC (Model of Acidification of Groundwater In Catchments; Cosby et al, 1985) is explicitly designed to perform long term simulations of changesin soilwater and streamwater chemistry in response to changes in acidic deposition. The processes on which the model is based are:

anion retention by catchment soils (e.g. sulphate adsorption):
adsorption and exchange of base cations and aluminium by soils;
alkalinity generation by dissociation of carbonic acid (at high CO_2 partial pressures in the soil) with subsequent exchange of hydrogen ions for base cations;

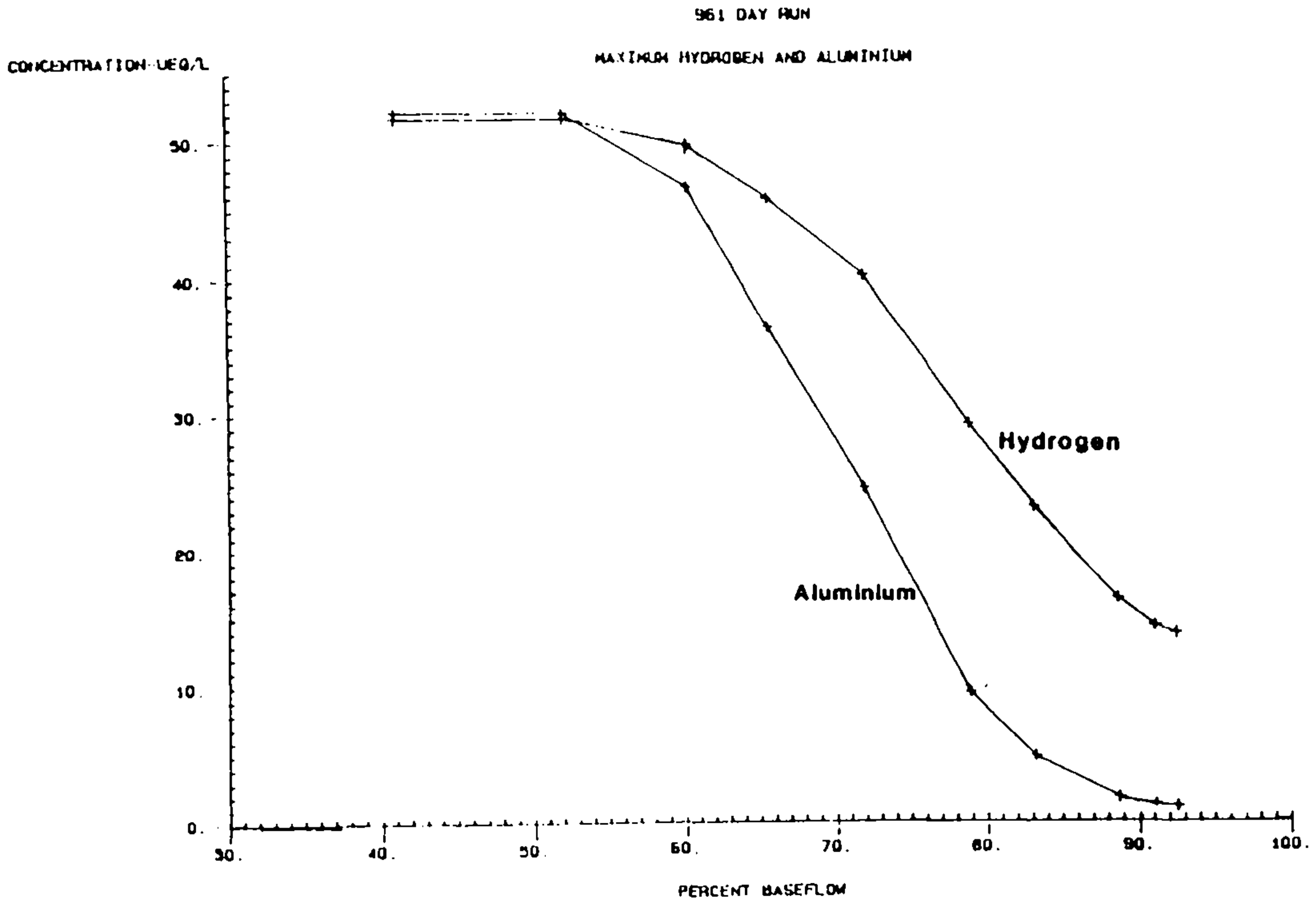


Figure 3

Maximum H^+ and Al^{3+} concentrations in the stream showing variation over a range of baseflow conditions (Three Year Simulation 1977-1980)

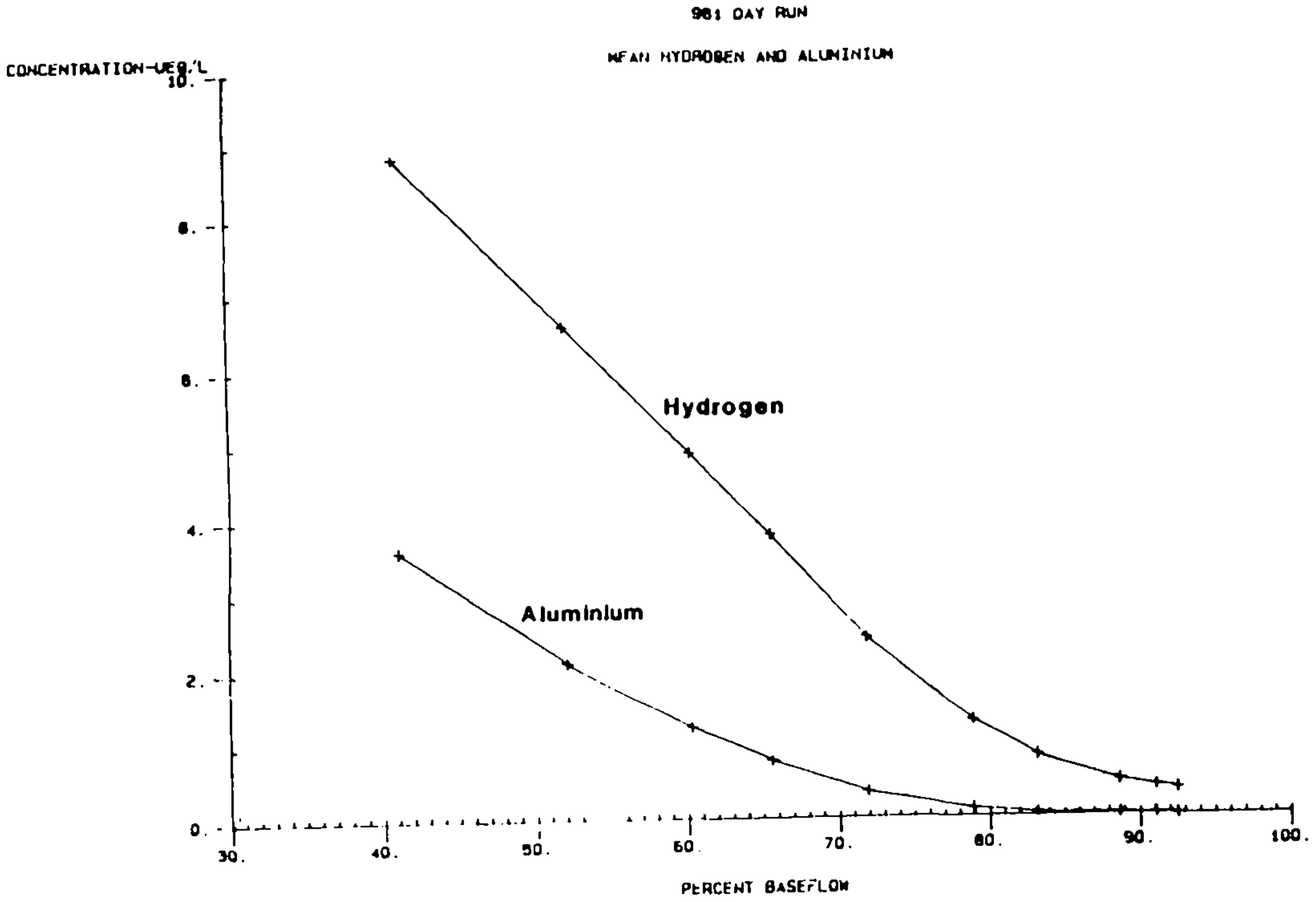


Figure 4

Mean H^+ and Al^{+++} concentrations in the stream showing variation over a range of baseflow conditions (Three Year Simulation 1977-1980).

weathering of minerals in the soil to provide a source of base cations;
control of Al^{3+} concentrations by an assumed equilibrium with a solid phase of $Al(OH)_3$.

A sequence of atmospheric deposition and mineral weathering is assumed for MAGIC. Current deposition levels of base cations, sulphate, nitrate and chloride are needed along with some estimate of how these levels had varied historically. Historical deposition variations may be scaled to emissions records or may be taken from other modelling studies of atmospheric transport into a region. Weathering estimates for base cations are extremely difficult to obtain. Nonetheless, it is the weathering process that controls the long term response and recovery of catchments to acidic deposition and some estimate is required.

The MAGIC program has been applied to the Dargall Lane sub-catchment in Loch Dee and a detailed description of the application is given by Cosby et al (1986).

Several chemical, biological and hydrological processes control stream water chemistry. These processes are often interative and not easily identifiable from field observation. Modelling allows separation of the different factors and the establishment of their relative importance quantitatively. Here the factors considered are afforestation, dry and occult deposition, variations in acidic oxide loading and deforestation.

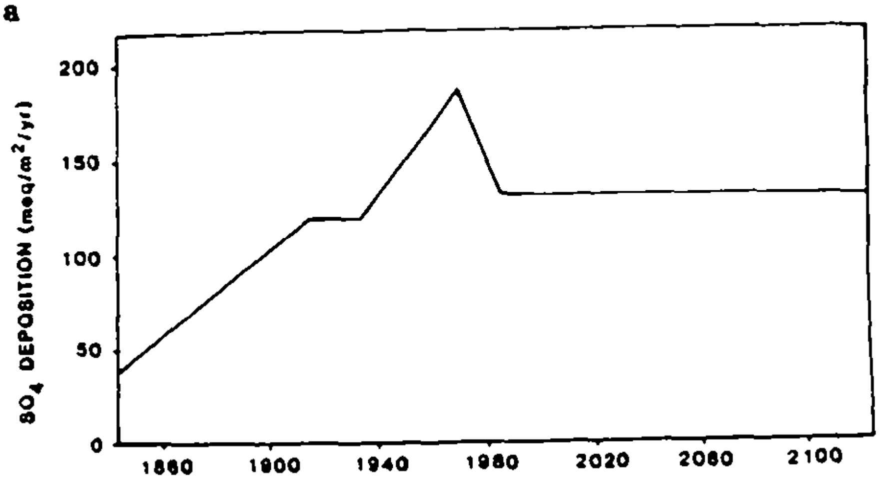
LONG TERM ACIDIFICATION TRENDS FOR DARGALL LANE

Figure 5 shows a simulation of long term acidity for the Dargall Lane catchment. The sulphate deposition history is shown in Figure 5a and this 'drives' the MAGIC model. The historical simulation of pH shown in Figure 5b is similar to the values obtained from the diatom records of lochs in the region in that a significant decrease in pH from 1900 onwards is inferred (Batterbee et al, 1985, Flower et al, 1983). The steeper decline from 1950 to 1970 follows from the increased emission levels during this period. The model can also be used to predict future stream water acidity given different future deposition levels. For Dargall Lane stream acidity trends are investigated assuming two scenarios for future deposition. Firstly assuming deposition rates are maintained in the future at 1984 levels, the model indicates that annual average stream pH is likely to continue to decline below presently measured values. Second, assuming deposition rates are reduced by 50% from 1984 levels (between 1985 and 2000) the results indicate that current stream water acidity will be maintained (Figure 5b). Further details of the application of this model are given elsewhere (Cosby et al, 1986). Note an increase in stream water pH about 1980; this follows a significant drop in sulphur emissions during the 1970s. Note also that an earlier decline in streamwater acidity is predicted if there had been no reductions in emissions since 1970.

AFFORESTATION

Afforested systems are more complex to model than grassland systems because the introduction of the forest pertubs a grassland ecosystem which in itself is difficult to model. The effects of the forest root system, leaf litter layer and drainage ditches will change the hydrological

5a



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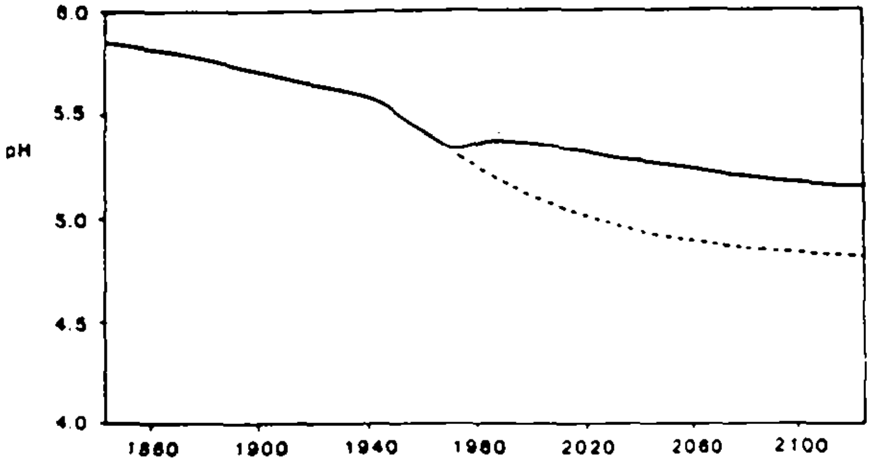


Figure 5a

Sulphate deposition history used as input for the MAGIC reconstruction of pH in the Dargall Lane moorland catchment

5b

Simulation of the pH of streamwater in the Dargall Lane moorland catchment assuming three sulphate deposition scenarios

—— Historical levels to 1984 and constant 1984 levels thereafter (see Figure 2a)

Historical levels to 1984 and 1984 levels reduced by 50% by the year 2000 and constant thereafter

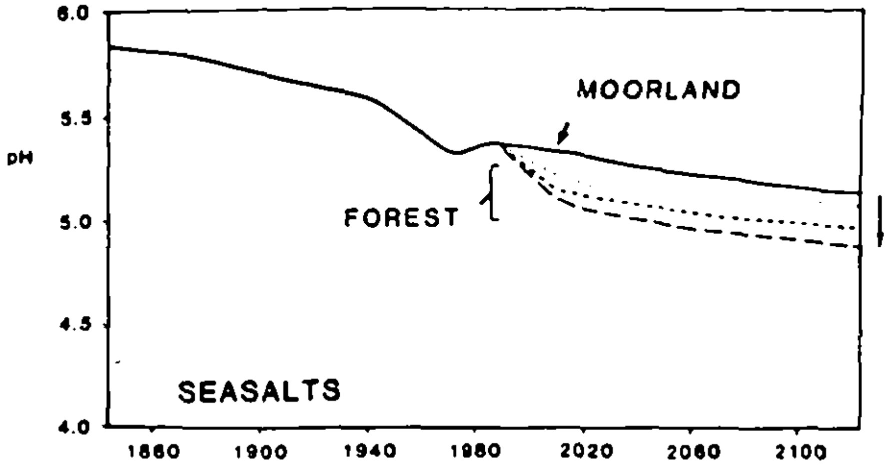
---- Historical levels to 1970 and constant 1970 levels thereafter.

pathways; this will control the nature and extent of the chemical reactions in the soil and bedrock. Further, the additional filtering effect of the tree on the atmosphere will enhance occult/particle deposition and evapotranspiration will increase the concentration ofdissolved components entering the stream. The magnitude of these different effects varies considerably; for example evapotranspiration from forests in the British Uplands is typically of the order of 30% of the precipitatation which is almost twice the figure for grassland. This will have the consequence that the total anion concentrations within the stream and soil waters increase by 14% following afforestation. The forest will also increase anion and cation loading due to the enhanced filtering effect of the trees on air and occult sources. [Several forest catchment studies have shown that Chloride concentrations are higher in streamwaters than in the corresponding rainfall or grassland streams. Such a difference results from dry and occult deposition assuming that chloride is derived from a maritime source and not from leaching from the catchment bedrock. Such increases are typically of the order of 30%]. The filtering effects will apply both to marine and pollutant aerosol components. Altering the hydrological pathways can also have a major effect on stream water quality since the forest tends to increase surface runoff thereby flushing/ displacing highly acidic water from the surface layers; the soil zone acts as a proton and aluminium source whilst the bedrock, if silicate or carbonate bearing, provides proton consumption by weathering reactions.To illustrate the effects of afforestation simply in terms of increased concentrations from both enhanced dry deposition and evapotranspiration, the MAGIC model has been applied to the Dargall Lane catchment assuming that a forest is developed over the next 40 years. It should also be noted that, here, no allowance has been made for the effects of cation and anion uptake by the trees during their development; the incorporation of base cations into the biomass would result in an enhanced acidification effect during this period.

Of critical importance is the relative and absolute contribution of marine and pollutant inputs from dry and occult deposition. Figure 6 shows the effects of increasing evapotranspiration from 16 to 30% over the forest growth period with varying levels of marine, pollutant and marine + pollutant inputs. Increasing either marine or pollutant components leads to enhanced stream water acidity, the greatest effects being observed when both components are present; the effect of simply increasing evapotranspiration from 16 to 30% has a similar effect but the changes are much smaller. The important features of these results are the enhanced and acidic oxide inputs from increased scavenging by the trees result in a marked reduction in pH levels and that there is an additive effect when both processes are combined. These reductions are much greater than the effect of evapotranspiration.

ATMOSPHERIC ACIDIC OXIDE INPUTS

An important factor in determining stream acidity in the upland UK is the level of acidic oxide deposition; rates of deposition (non marine wet deposition and dry deposition)[14-15] can vary from 0.5 to over 6 g S $m^{-2}yr^{-1}$ and from 0.1 to over 0.5 g N $m^{-2}y^{-1}$. Figure 7 shows the effects of such variations for both moorland and forested catchments; the highest levels correspond to areas with high atmospheric acidic oxide rates (3 times the historic and 1984 deposition levels observed in the Southern Uplands of Scotland). With increasing atmospheric acidic oxide pollution, 6 a



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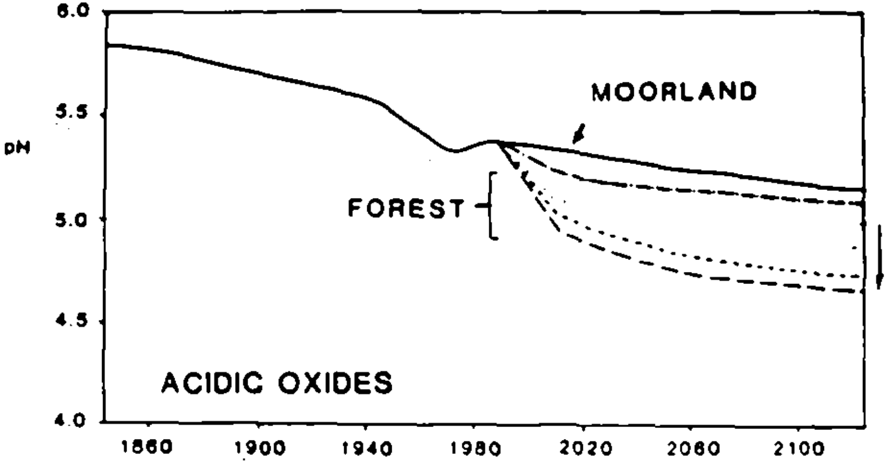

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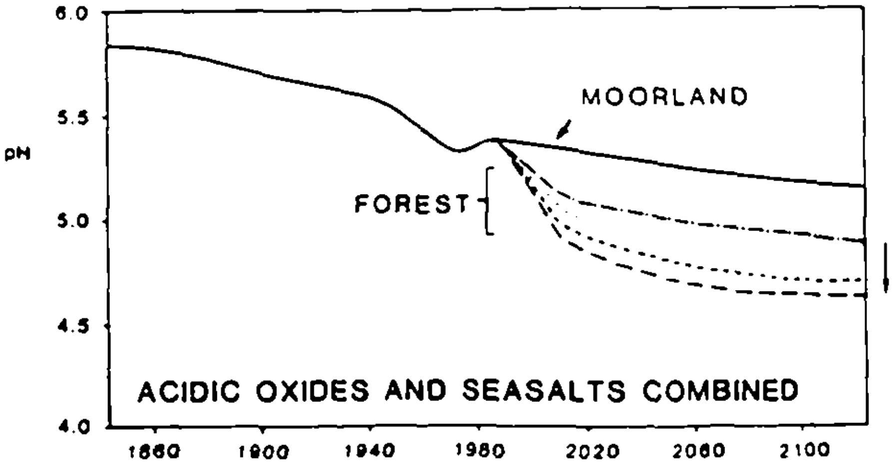

INCREASING DRY/OCCULT DEPOSITION

Figure 6

(a) Simulation of the pH of the streamwater from the Dargall Lane catchment comparing the moorland catchment response assuming Figure 2a deposition rates (——), the effect of 14% additional evaporation following afforestation (··   ), the effect of 14% additional evaporation plus 15% additional input of natural seasalts following afforestation in 1985 (-·-·-·), and the effect of 14% additional evaporation plus 30% additional input of natural seasalts following afforestation in 1985 (- — —)

(b) Simulation of the pH of streamwater from the Dargall Lane catchment comparing the moorland response (——) to the forested catchment response assuming increased evaporation (-·-·-) with different levels of pollutant scavenging (····, 20% additional sulphate, ----, 40% additional sulphate, — — —, 60% additional sulphate)

(c) Simulation of the pH of streamwater from the Dargall Lane catchment showing the moorland response (——) and the combined effects on the forested catchment of increased evapotranspiration, increased scavenging of natural sea salts, and various levels of increased scavenging of pollutant inputs (-·-·, zero additional pollutant scavenging, ·   20% pollutant scavenging, ----, 40% pollutant scavenging, — — —, 60% pollutant scavenging).

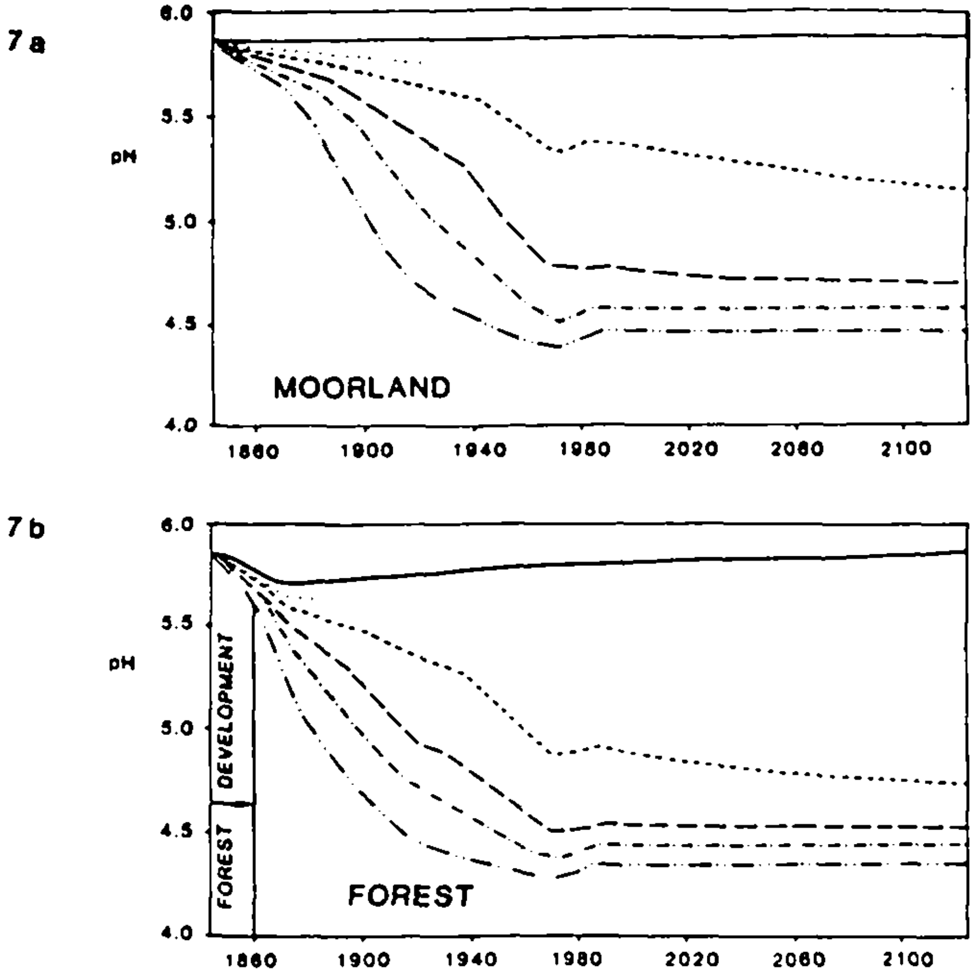

Figure 7

(a) Simulation of the pH of streamwater from the Dargall Lane moorland catchment assuming sulphate deposition patterns (shown in Figure 5a) modified by various factors to reproduce a range of loading conditions (i.e. from pristine to heavy pollution)

(b) Simulation of the pH streamwater from the 'forested' Dargall Lane catchment assuming afforestation from 1844 onwards and sulphate deposition patterns (see Figure 5a) multiplied by various factors to reproduce a range of loading conditions from pristine to heavy pollution.

—— Background rates (pristine conditions)

0.5 x Figure 5a deposition concentrations (low pollution)

---- 1 x
— — — 1·5 x } intermediate pollution

-·-·- 2 x
-··-··- 3 x } heavy pollution

the decline in stream pH is accelerated, the changes occur much earlier, and the final pH of the stream water is lower.

DEFORESTATION

Whilst afforestation increases stream acidity, as shown both by the model predictions and field evidence, then deforestation will result in a reduction in stream water acidity. Figure 8 shows the effects of deforestation from the present time for a range of acidic input loadings. The result shows that while there is a short term improvement in stream acidity, the long term acidification trend is maintained. It is interesting to note that the recovery following deforestation at the intermediate deposition levels is greater than that at the higher levels. This is because base saturation has not been completely depleted, and the reduced deposition following deforestation can be buffered by the available cations. Under the higher deposition levels base saturation is reduced to very low levels making recovery much less significant. Note that afforestation following tree harvesting will negate the improvement in stream water acidity.

IMPLICATIONS

The modelling enables assessment of the relative effects of atmospheric acidic oxide pollution and conifer afforestation, as well as highlighting some of the topics that need further consideration. For example, the long term trends in stream water acidification for the grassland catchment suggest that for at least part of the upland UK, acidic oxide pollutant inputs are the dominant source of increased stream water acidity. The model predictions are similar to observations of stream acidity found in Southern Scandinavia and add weight to the conclusion that such pollutant inputs are also a major source of stream acidification in those countries as well. How important this acidification process is on a regional basis in the upland UK cannot be gauged immediately because many unresolved factors remain, as mentioned above. However, much of the British uplands have soils which are susceptible to acidic inputs; it is therefore reasonable to assume the results of this present modelling exercise are widely applicable. If the above results are representative of sensitive upland areas then reductions in present acidic emissions of the order of 50% are required to prevent further increase in stream acidity moorlands; afforested catchments require greater reductions. The study points to the need for further regional analysis of soil and stream water chemistry, as well as a better understanding of hydrogeochemical processes operating within catchments. Further, the study provides an example of the need to establish the extent of scavenging of aerosols onto plant surfaces, and more generally on the benefits of multidisciplinary catchment studies. Finally, the detrimental effect on stream water quality caused by conifer afforestation in uplands subject to acidic deposition is irrefutable. While there is uncertainty regarding the nature and the extent of the hydrogeochemical processes operative there is a need to change existing forestry practices which are of immediate pragmatic concern.

5. CONCLUSIONS

The model techniques applied at IH have proved to be particularly useful yielding information on the catchment responses, processes and possible future behaviour.

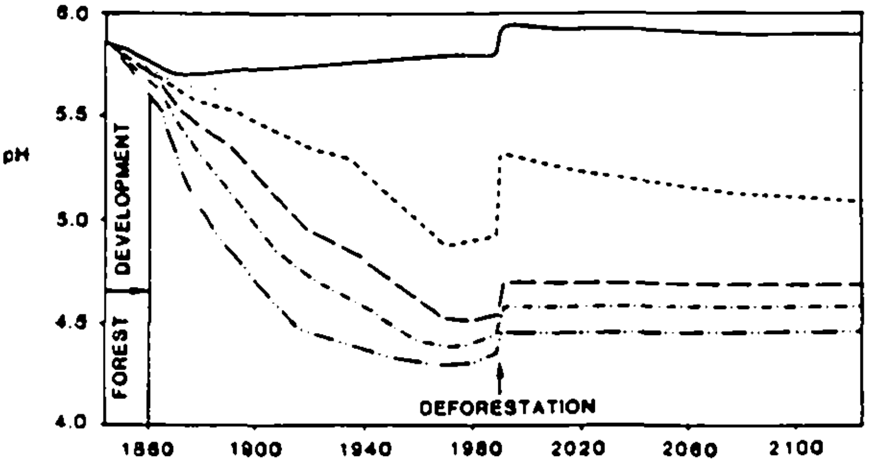

Figure 8

Simulation of the pH of streamwater for the Dargall Lane catchment assuming afforestation from 1844 and deforestation in 1990. Deposition patterns as described in Figure 7.

On the hydrological side time series techniques, lumped and distributed hydrological models are available. In the case of chemical processes, time series techniques can be applied but the principal models available at IH are the BIRKENES and MAGIC models. Modifications such as the introduction of sea salt will be necessary in the case of the BIRKENES model before application to the Loch Dee and Plynlimon catchments is possible. Also it may be necessary to reassess the dominant equilibria used in the model; forexample is aluminium controlled by $Al(OH)_3$, $Al(OH)SO_4$ or by $Al(OH)_{1-x}SiO_{2x}$

We hope to develop a modified and combined BIRKENES and MAGIC chemistry and couple this with the distributed models to provide an additional tool with which to investigate catchment behaviour.

ACKNOWLEDGEMENTS

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SECTION 6 - AGROCHEMICAL POLLUTION AND ASSOCIATED MODELLING PROBLEMS

TABLE OF CONTENTS

1.1 Introduction

The use of toxic chemicals as the principal weapon against pest and disease attack, and against weeds is commonly regarded as one of the most worrying developments in modern agriculture (DOE, 1979). The quantities of chemicals used continues to rise, as will be seen later, hence this concern continues. In the context of this report, the word "pesticides" is used in the generic sense and includes insecticides, fungicides, herbicides, and other categories of compounds used to kill pest. The development of modern pesticides, while undeniably a triumph in science and technology has not been without its problems (McEwen and Stephenson, 1979). Problems such as resistance, persistence and damage to non-target organisms, for example. These and others will be investigated in this report in relation to their effects upon river water quality.

Today more than 1000 pesticide chemicals are in common use around the world, of which more than 250 are commonly used in agriculture (Ware, 1983). Only a few of these persist for more than a few weeks or at most months in soil or water, and of those that do most are the organochlorine insecticides, which include aldrin, dieldrin, chlordane, dicofol, endosulfan, endrin, lindane, DDT, heptachlor and toxaphene (Edwards, 1973).

During the 1950's and 1960's reports of large residues of these organochlorine pesticides in soils, and small amounts in water and in stream sediments, began to appear in the literature (Edwards, 1973). These discoveries began to cause concern about their long-term ecological effects and has since resulted in a move away from the use of these more persistent pesticides, towards an increasing use of less persistent organophosphorous and more recently, pyrethroid pesticides; a trend witnessed throughout the developed world at least (DOE, 1979; Ware, 1983; Garman and Sutherland, 1983).

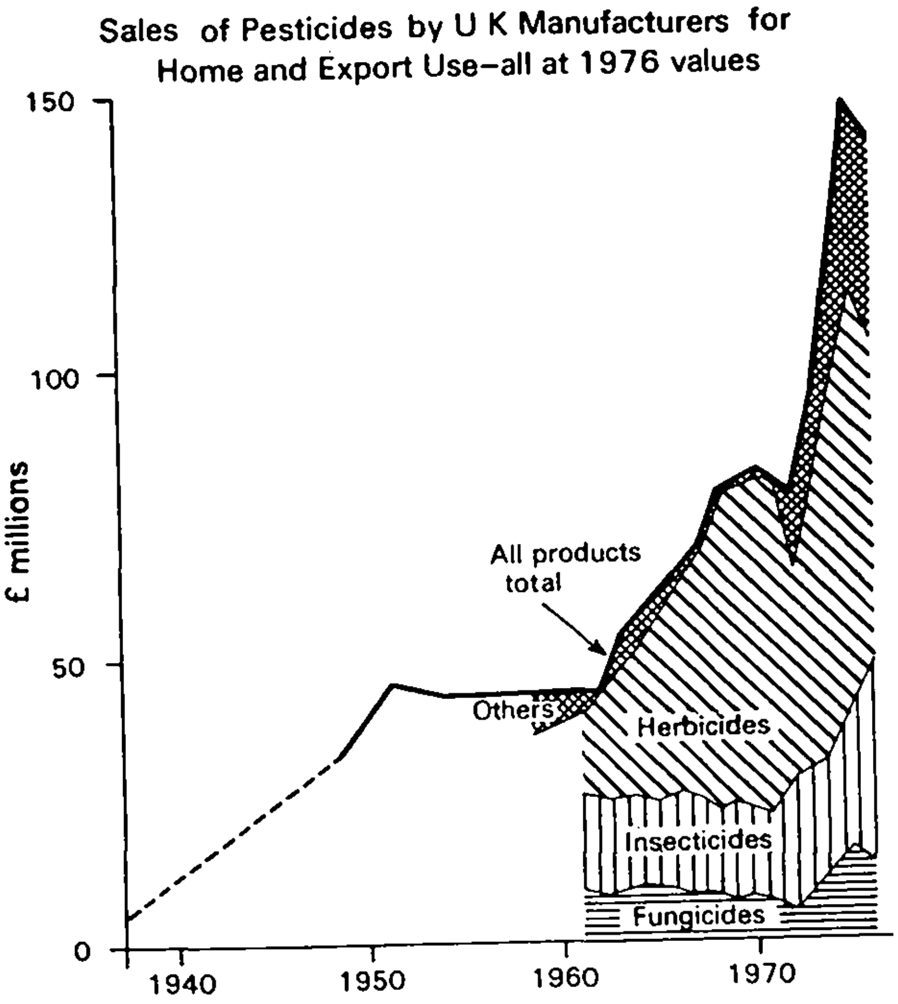
Lastly, although pesticides are chiefly used in agriculture, they are also found elsewhere in homes and gardens, in industry, and in public health. These non-agricultural uses have been investigated by the Department of the Environment (DOE, 1974). For example, it appears that some pesticides (e.g. dieldrin) are now used in moth-proofing and wood preservation much more than they are in agriculture.

1.2 Pesticide usage in the United Kingdom

Up to 1945, chemical control of pests in England and Wales was mostly by a very limited number of chemicals (Perring and Mellanby, 1977). At that time, few pesticides were pest specific and their selectivity was usually a matter of timing, while their use was mainly confined to high value crops such as fruit, hops, market garden and glasshouse crops.

During the second World War, the organochlorine insecticides, DDT and HCH and the translocated herbicides, 2,4 - D and MCPA were developed and in the late 1940's these became available for use in British agriculture. By 1950, 15 pesticides (apart from herbicides) were approved by the Ministry of Agriculture and Fisheries (MAFF), as seen in Table 1 (DOE, 1979). By 1955 the list included 27 pesticides (including herbicides). And in 1960 it included 47, while in 1965 it listed 98. Chemicals introduced in the 1960's included: aldrin, dieldrin, endosulfan, endrin and other organochlorine insecticides, as well as many new contact herbicides such as dinoseb, paraquat and diquat (Perring and Mellanby, 1977). The 1970 Approvals List included 163 chemicals and by 1975, 200 were listed, newcomers including: aldicarb and systemic fungicides such as carboxin.

DOE (1979), summarised the growth of approved products as formulations, for the period 1944 to 1976 (Table 2). Also, the Pesticides Survey Group of MAFF has been surveying usage of pesticides on crops in England and Wales since 1965, Sly (1977) providing a review for the period 1965 to 1974. The annual usage in terms of treated area and the area of crops grown is shown in Table 3. The estimated quantities of active ingredient used are shown in Table 4. There has been a reduction in the use of organochlorine insecticides since the first review of these persistent pesticides, but up until 1977 only endrin was deleted from the Approvals List. Most of the expansion in availability of insecticides in the 1970's has thus been of contact or organophosphorous insecticides and of carbamate insecticides and acaricides.



Sales of Pesticides by U K Manufacturers for Home and Export Use–all at 1976 values

Figure 1.
Sales of Pesticides by UK Manufacturers for Home and Export use – all at 1976 values

TABLE 1

Chemicals in Approvals List of MAFF, 1950 to 1975

Chemical	Number listed					
	1950	1955	1960	1965	1970	1975
Natural insecticides	1	3	3	2	2	2
Contact organophosphorus insecticides	-	3	3	3	10	20
Systemic organophosphorus insecticides	-	-	3	2	16	15
Organochlorine insecticides	2	2	6	8	9	7
Organochlorine acaricides	-	-	4	4	4	3
Carbamate insecticides, acaricides	-	-	-	1	3	8
Other insecticides, acaricides	4	5	6	4	5	5
Systemic fungicides	-	-	-	-	4	11
Fungicides (powdery mildew)	-	-	-	3	4	5
Dithiocarbamate fungicides	-	1	1	7	10	10
General fungicides	1	1	3	5	8	13
Elemental fungicides		5	5	5	7	7
Mainly contact herbicides		2	3	8	14	19
Mainly soil herbicides		1	2	10	35	39
Mainly translocated herbicides		2	6	14	16	20
Soil fumigants		1	1	3	8	8
Molluscicides				1	2	2
Growth regulators				3	6	6

Source: SLY.J.M.A. in Ecological Effects of Pesticides, Academic Press London 1977, p2, (in DOE, 1979).

TABLE 2

Chemicals in Approvals List of MAFF, 1950 TO 1976

Year	Number of products
1944	63
1948	216
1952	352
1956	446
1960	532
1964	540
1968	783
1972	810
1976	819

Source: SLY.J.M.A. in Ecological Effects of Pesticides, Academic Press London 1977, p3. (in (DOE,1979).

TABLE 3

Recent data on extent of pesticide treatment of crops

England and Wales

Crop group	Year of survey	Area of crops grown (hectares)	Percentage of crops treated
Cereals	1974	3,245,845	99.5
Potatoes, sugar beet and field beans	1974	434,439	98.4
Fodder, forage and seed crops	1974	1,649,484	44.8
Vegetables	1972	221,433	94
Orchards	1973	50,355	92
Hops	1975	6,414	100
Soft fruit	1975	13,123	99
Glasshouse crops	1972	3,639	97.1
Hardy nursery stock	1971	6,500	87

(Source: Ministry pesticide survey, in DOE (1979)).

TABLE 4

Types of pesticides used in agriculture and horticulture. Estimated annual average quantities of active ingredient 1971-5 England and Wales

Pesticide group	"Spray hectares" (a)	Tonnes of active ingredient per year
Insecticides		
Organochlorine compounds	148,105	132
Organophosphorus compounds	844,011	419
Other insecticides	117,232	779
Seed treatments	3,717,621	565
Fungicides	1,896,538	2,194
Herbicides	6,020,624	15,712
Other pesticides	49,438	1,960
Total	12,645,212	(b)

(Source: Ministry pesticide surveys, in DOE (1979))

The biggest changes in fungicides involved the introduction of systemic fungicides in the late 1960's. Their greater efficiency having led to economic control of a variety of plant diseases. Also, the number of herbicides available up to 1976 increased about 2 times, partly as a result of new chemicals with general herbicidal activity and also partly due to the increased use of chemicals to control grass weeds in cereals.

Thus, the trends in pesticide usage up to 1976 can be roughly summarised in the form of a graph of sales in the UK (Figure 1). However, it appears that, in 1976, nearly 50 per cent of sales by value were exported. While, of that sold inside the UK, nearly 90 per cent were for use in agriculture and horticulture (DOE, 1979). But, there was an upward trend in sales of pesticide reflecting increased usage and not merely increased costs (DOE, 1979). More recent data on pesticide usage for 1977 are presented in Tables 5, 6 and 7 (DOE, 1979).

What is not apparent from these tables is the declining use of organochlorine compounds in agriculture. In addition, there is evidence of a substanial increase in the use of herbicides on certain crops and a recent increase of insecticide use on cereals. Indeed, herbicides form the majority of pesticides applied and are now used on virtually all agricultural and horticultural crops grown on any scale, crops often receiving two or more applications. It has been estimated (Fryer, 1977) that the total area of agricultural land in the UK treated with herbicides is in the range of 4.2 to 5.4 million hectares.

Since 1977, Sly has published two other reviews of pesticide usage (Sly 1981 and 1985). First, for the period 1975 to 1979 (Sly, 1981) Table 8, gives a comparison of their usage on agricultural and horticultural crops. There was little overall change in usage of the organochlorines and the increased usage of organophosphorous insecticides was mostly on cereals to control aphids. The large increase in the area treated with other insecticides, acaricides and molluscicides was mostly the increased usage of pirimicarb to control cereal aphids and increased usage of aldicarb, methiocarb and the synthetic pyrethroids. There were no substantial changes in usage of seed treatments apart from the replacement of persistent aldrin or dieldrin/mercury on cereals and sugar beet with other formulations.

TABLE 5

Types of pesticides used on cereals, 1974 and 1977
Estimated quantitites of active ingredients, England and Wales

Pesticide groups	Spray hectares 1974	Spray hectares 1977	Tonnes of active ingredients 1974	Tonnes of active ingredients 1977
Insecticides				
Organochlorine compounds	0	1,000	0	1
Organophosphorus compounds	41,000	294.000	17	107
Other insecticides	5,000	272,000	1	43
Seed treatments	3,309,000	3,358,000	553	480
Fungicides	616,000	978,000	394	588
Herbicides	4,475,000	4,408,000	8,727	8,026
Other prestícides	67,000	188,000	84	263
Total	8,513,000	9,499,000		

(Source: Ministry pesticide surveys)

TABLE 6

Types of pesticides used on other arable crops. *1974 and 1977
Estimated quantities of active ingredients, England and Wales

Pesticide groups	Spray hectares 1974	Spray hectares 1977	Tonnes of active ingredients 1974	Tonnes of active ingredients 1977
Insecticides				
Organochlorine compounds	30,000	40,000	22	35
Organophosphorus compounds	469,000	274.000	191	99
Other insecticides	19,000	180,000	36	416
Seed treatments	433,000	430,000	2	2
Fungicides	599,000	616,000	696	882
Herbicides	648,000	918,000	4,835	6,131
Other prestIcides	0	0	0	0
Total	2,198,000	2,458.000		

(Source: Ministry pesticide surveys)
*potatoes, sugar beet, field beans, rape, mustard.
Source: DOE (1979)

TABLE 7

Frequency of pesticide treatment*

Estimated percentage of planted area of arable crops receiving particular total numbers of annual treatments

England and Wales, 1977

	Area planted (hectares)	Number of treatments received			
		0	1-3	4-6	7-more
Cereals	3,209,329	1%	55%	42%	2%
Other arable crops	476,261	1%	43%	46%	10%

(Source: Ministry of pesticide surveys)
*Including seed treatment

The biggest changes in fungicides involved the introduction of systemic fungicides in the late 1960's. Their greater efficiency having led to economic control of a variety of plant diseases. Also, the number of herbicides available up to 1976 increased about 2 times, partly as a result of new chemicals with general herbicidal activity and also partly due to the increased use of chemicals to control grass weeds in cereals.

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TABLE 8 **Estimated annual usage of pesticides in agriculture and horticulture in England and Wales, 1971-9174 and 1975-1979 (spary hectares and tonnes of active ingradients)**

Pesticide	1971-1974		1975-1979	
	Spray hectares	Tonnes	Spray hectares	Tonnes
OC insecticides, acaricides	148,000	131	146,000	166
OP insecticides	845,000	430	975,000	534
Other insecticides, acaricides, molluscicides	93,000	1,286	597,000	907
Seed Treatments	3,718,000	565	3,753,000	591
Fungicides	1,895,000	2,400	2,253,000	2,336
Herbicides, defoliants	6,003,000	15,250	7,868,000	19,925
Other pesticides	81,000		203,000	1,038

*including chemicals for burning-off

Source: Sly (1981)

However, there was an overall increase in usage of fungicides mainly due to a large increase in usage of systemic fungicides. The apparent large increase in usage of herbicides is mainly accounted for by the 1.8 m ha of grassland which were treated in 1979, with no comparable data avilable for the period 1971-1975. But there was an increase in the usage of total herbicides such as paraquat and glyphosate, mostly for stubble clearing, and of herbicides for the control of grass weeds in cereals.

Usage of pesticides on each group of crops (1975-1979) is summarised in Table 9 (Sly, 1981). Other arable crops consisted mostly of potatoes, sugar beet, field beans, mustard and rape grown as seed crops. Although not included in Table 9, the comparative figure for usage in Forestry in 1978 is 0.04 applications. Overall usage varied considerably and is shown below:

Crop Group	Mean number of pesticide applications
Fodder/forage crops (mostly grass)	0.4
Cereals	3.0
Vegetables	3.9
Other arable crops	4.8
Hardy nursery stock	6.1
Glasshouse crops	8.1
Soft fruit	8.7
Orchards	17.1
Hops	23.4
* Forestry	0.04

* 1978 only

In terms of spray area, the most extensive usage was of seed treatments and translocated herbicides (both mainly to cereals). The largest tonnages of active ingredients were dithiocarbamate fungicides (mostly on potatoes), herbicides and sulphuric acid used at high rates of active ingredient per acre on about one-fifth of main crop potatoes.

TABLE 9 Annual usage of pesticides in agriculture and horticulture, England and Wales, 1975-1979 spray hectares and tonnes of active ingredients

	Soft fruit 1975		Glasshouses 1976		Hardy nursery stock 1976		Vegetables 1977		Cereals 1977	
	ha				ha					
Insecticides, molluscicides, acaricides										
Organochlorines	15,902	14.58	3,075	3.01	2,926	3.62	41,378	40.07	813	1.02
Contact organophosphates	4,875	5.76	4,310	6.06	1,792	2.02	119,511	109.46	6,551	4.20
Systemic organophosphates	10,275	3.57	1,862	0.72	7,937	2.30	174,663	104.60	287,476	121.84
Carbamates	2,035	1.22	3,253	6.53	982	1.40	30,406	36.44	269,082	73.91
Others	1,267	39.85	4,773	9.98	312	17.87	301	0.24	3,011	2.83
Total	34,354	64.98	17,273	26.30	13,949	27.21	366,159	290.81	566,933	203.80
Insecticide/fungicide mixtures			738	0.83	3	trace				
Seed Treatments			7	trace	3	trace	161,671	64.60	3,272,918	496.88
Fungicides										
Systemic	12,763	8.19	5,068	7.42	4,505	2.85	24,277	16.05	910,171	461.67
Mainly against powdery mildews	10,991	13.72	808	0.56	3,336	2.70	194	0.10	2,212	1.66
Dithiocarbamates	7,851	20.74	13,594	55.03	1,738	2.93	9,556	13.82	28,438	49.19
Others	19,459	38.23	2,392	33.23	2,460	5.57	7,062	6.00	36,004	56.01
Total	51,064	80.88	21,862	96.24	12,039	15.05	41,089	35.97	976,825	568.53
Herbicides, defoliants										
Mainly contact	5,791	5.01	135	0.16	3,451	3.46	118,110	280.05	542,560	811.57
Mainly soil-acting	19,530	70.17	447	1.05	7,369	17.26	262,149	515,81	588,370	1,203.77
Mainly translocated	3,825	9.30	1	trace	764	2.23	13,087	17.98	3,455,691	5,566.79
Sulphuric acid							2,048	345.29		
Tar oil										
Total	29,146	84,48	583	1.21	11,584	22.95	395,394	1,159,13	4,576,621	7,582.13
Growth regulators			904	1.53	42	trace	2,981	10,43	188,136	238.93
Soil sterilants, fumigants	17	trace	2,013	610.22	153	47.65	203	79.84		
Total area treated	114,581	230,34	43,380	736.33	37,773	112.86	967,497	1,640.78	9,581,433	9,090.27
Area grown	13,123		5,350		6,156		250,702		3,209,331	

Source: Sly (1981)

TABLE 9 Annual usage of pesticides in agriculture and horticulture, England and Wales, 1975-1979 spray hectares and tonnes of active ingredients
Continued

	Other arable crops 1977		Foffer/forage 1979		Orchards 1979		Hops 1979		Total	
	ha		ha		ha	t	ha	t	ha	
Insecticides, molluscicides, acaricides										
Organochlorines	40,061	51.07	3,728	5.81	21,551	23.26	16,918	23.42	146,252	165.85
Contact organophosphates	9,688	6.14	2,341	2.34	30,305	26.72	10,212	10.20	189,585	172.90
Systemtic organophosphates	264,709	106.68	1,512	0.26	32,161	12.72	4,923	8.49	758,518	361.18
Carbamates	173,740	158.63	6,267	1.36	13,183	23.36	10,586	12.15	509,534	314.00
Others	6,009	3.37	4,913	4.57	63,270	513.58	3,539	0.52	87,395	592.81
Total	494,207	325.89	18,761	14.34	160,470	598.64	46,178	54.78	1,718,284	1,606.75
Insecticide/fungicide mixtures									741	0.83
Seed Treatments	235,084	8.87	82,974	20.57					3,752,657	590.92
Fungicides										
Systemic										
Mainly against powdery mildews	8,985	5.58	23,383	9.69	69,105	33.66	26,460	5.51	1,084,717	550.62
Dithiocarbamates		.	.	.	172,077	128.18	3,027	1.34	192,645	148.26
Others	513,526	770.81	2,329	4.34	12,742	29.46	20,657	58.63	610.431	1,005.94
	93,861	56.39			187,707	374.01	16,206	61.79	365,151	631.23
Total	616,372	832.78	25,712	14.03	441,631	565.31	66,350	127,27	2,252,944	2,336.05
Herbicides, defoliants										
Mainly contact	297,890	348.17	112,621	39.03	16,654	6.84	8,356	11.02	1,105,568	1,505.31
Mainly soil-acting	501,799	890.66	123,439	181.09	31,481	46.80	3,983	7.12	1,538,567	2,933.73
Mainly translocated	85,343	148.66	1,557,032	842.14	77,682	116.05	1,761	3.25	5,185,186	6,706.38
Sulphuric acid	33,081	8,171,01					.	.	35,129	8,516.30
Tar oil							5,977	265.58	5,977	265.58
Total	918,113	9,558.50	1,793,092	1,062.26	125,817	169.69	20,077	286.95	7,870,427	19,927.31
Growth regulators					7,770	3.65	803	trace	200,636	254.54
Soil sterilants, fumigants	208	45.76							2,594	783.47
Total area treated	2,263,984	10,771.80	1,920,539	1,111.20	735.688	1,337.29	133,408	469.00	15,798,203	25,499.87
Area grown	476,117		5,327,950		42.916		5,706		9,337,351	

Source: Sly (1981)

The most extensive areas treated with insecticides, acaricides and molluscicides were with demeton-s-methyl and dimethoate to most crops, and pirimicarb especially upon cereals. About two-thirds of all seed treatments included mercury, about 80 percent of cereals and all sugar beet seed being so treated. Also large quantities of ethirimol and HCH/mercury were used as seed treatment. The most extensive areas treated with fungicides were with tridemorph, carbendazim, "Dithane" (either mancozeb or zineb), and benomyl. Apart from Dithane (used mostly on potatoes) these fungicides are all systemic. The systemics were mostly applied to cereals, the dithio carbamates to potatoes and captan and sulphur to fruit and hops. In terms of quantity of active ingredients, usage of eight fungicides exceeded 100 tonnes. These were mancozeb, tridemorph, captan, zineb, sulphur, maneb, carbendazim/maneb and propineb. Lastly the usage of herbicides is complicated because many of them are formulated as mixtures, but the most widely used active ingredients were dicamba, dichlorprop and mecoprop, mostly alone. Similarly, the quantities of active ingredients are obscured by mixtures but extensive quantities of most of the above were used.

As nearly 400 pesticides or formulated mixtures of pesticides were recorded during 1975-1979 it is not feasible to compare the changes in use of each of them. The most important are shown in Table 10 (Sly, 1981). Of the insecticides, there were very large increases in usage of aldicarb, pirimicarb and dimethoate on most crops and a large increase in triazophos usage, mostly on brassicas. The increased usage of methiocarb was mostly on arable crops. There was also evidence, towards the end of the survey of a large scale usage of synthetic pyrethroids (especially permethrin and decamethrin). Cereal seed treatments showed the withdrawal of aldrin/mercury and dieldrin/mercury and an increase in usage of HCH/mercury in their stead. On sugar beet, dieldrin/mercury has been replaced by methiocarb/mercury.

Changes in usage of fungicides are marked by large increases in systemic fungicides including the introduction of new chemicals such as triadimefon. The reduced use of maneb and fentin acetate maneb on potatoes has been matched by increased usage of mancozeb and of captafol. Lastly, several herbicides have shown increased usage, notably paraquat (and glyphosate) for total weed control, benazolin mixtures for broad leaved weed control in cereals, flamprop-isopryl, isoproturon and difenzoquat for control of grass weeds and trifluralin on brassicas.

TABLE 10 The more important usage of pesticides in 1971-1974 and 1975-1979 (spray area '000 ha) (Sly, 1981)

Pesticide	Usage in	
	1971-1974	1975-1979
INSECTICIDES, ACARICIDES, NEMATICIDES, MOLLUSCICIDES		
DDT	62	59
Triazophos	3	50
Demeton-S-methyl	337	408
Dimethoate	115	224
Aldicarb	3	89
Pirmicarb	29	316
SEED TREATMENTS		
Aldrin/mercury	22	0
Dieldrin/mercury	212	0
Chlorfenvinphs/mercury	106	73
Ethirimol	436	477
HCH/captan	42	99
HCH/mercury (single rate)	1,247	780
HCH/mercury (double rate)	144	173
Mercury	1,322	1,472
Methiocarb/mercury	10	203
FUNGICIDES		
Benomyl	45	120
Carbendazim	2	213
Triadimefon	0	121
Tridemorph	422	367
Dinocap	131	54
Mancozeb	242	293
Maneb	153	80
Dithian	95	71
Fentin acetate/maneb	133	64
HERBICIDES		
Bromoxynil/ioxynil/dichlorprop	100	179
Paraquat	229	379
Phenmedipham	114	155
Isoproturon	2	157
Tri-allate, di-allate	377	309
Barban	257	177
Benazolin mixtures	9	216
Benzoylprop-ethyl	164	220
2,4-D	210	193
Dicamba/MCPA	242	12
Dicamba/Mecoprop/MCPA	290	577
Dichlorprop	175	155
Dichlorprop/MCPA	162	29
Digenzoquat	7	254
Flamprop-isopropyl	1	108
MCPA	990	950
Mecoprop	710	644
2,4,5-T(alone)	6*	173
2,3,6-TBA/Dicamba/MCPA/mecoprop	200	269
Trifluralin	16	80
OTHER CHEMICALS		
Chlormequat	42	188
Maleic hydrazide	0.6	3
Methyl bromide	0.2	0.6

More recently, a review of pesticide usage for the period 1980 to 1983 has been published (Sly, 1985). A summary of usage on all crops in the periods 1971-74, 1975-79 and 1980-83 is shown in Table 11. The quantity of the organochlorine insecticides used in 1980-83 fell compared with 1975-79 although the area treated increased, mainly due to the usage of HCH on the greatly increased area of oilseed rape. The annual usage of DDT continued to drop from about 70 tonnes to about 34 tonnes in 1980-83, 31000 ha being treated compared with 59000 ha in 1975-79. There was little change in the usage of organophosphates. The use of carbamates increased dramatically mainly due to methiocarb being used to control slugs in cereals. There was a large increase in usage of pyrethroids on most crops, applied at low rate of active ingredients. The drop in quantities of applied seed treatments since 1979 arose from the replacement of ethirimol as a cereal seed treatment with other sytemic fungicides applied at much lower rates of active ingredients. There was a large overall increase in usage of fungicides, mostly from the increased usage of foliar-applied systemic fungicides to cereals. Most of the increased usage of herbicides meanwhile, was on cereals and other arable crops, although the greater area of grass included in the surveys in 1980-83 increased the treated area of grass. Expanded summaries of usage in 1980-83 are shown in Table 12 (treated hectares) and Table 13 (tonnes of active ingredients).

1.3 The chemistry of some commonly applied pesticides

There are several general classes of pesticides, as shown in the above tables. The most commonly used being the organochlorine, organophosphorous, carbamates and more recently synthetic pyrethroids. These can perhaps best be summarised by reference to some examples of the most commonly applied insecticides, fungicides and herbicides available in the U.K.

a) Insecticides

(i) Organochlorines

The organochlorines are insecticides that contain carbon, chlorine and hydrogen, the chlorine being substituted at various points on either a chain or ring structure of hydrocarbons. As a general rule, it has been shown that the more chlorine substitution, the better the chemical is as a pesticide, and also the more resistant it is to degradation. However,

TABLE 11 Estimated annual usage of pesticides oncrops in agriculture and horticulture in England and Wales, 1971-74, 1975-79 and 1980-83 (treated hectares and tonnes of active ingredients)

Pesticide	1971-74		1975-79		1980-83	
	Treated hectares	Tonnes	Treated hectares	Tonnes	Treated hectares	Tonnes
Organochlorines, insecticides, acaricides	148000	131	146000	166	160000	130
Organophosphate insecticides	845800	430	975000	534	923000	591
Pyrethroids	1000	<1	41000	2	172000	8
Other insecticides, acaricides, molluscicides	92000	1286	556000	905	956000	664
Seed treatments	3718000	565	3753000	591	3883000	301
Fungicides	1895000	2400	2253000	2336	6715000	4341
Herbicides, defoliants*	6003000	15250	7868000	19925	12402000	26340
Other pesticides	81000	2000	203000	1038	801000	3138
Area of crops and grass	563100^{a}		9322000		10511000	

* including chemicals for burning-off

a permanent grass was not included in 1971-1974

TABLE 12 Total annual usage of pesticides 1980-83 - treated area - hectares (Sly, 1985)

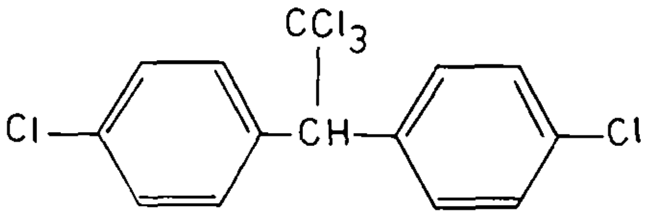
Chemicals	Soft fruit	Pro-tected crops	Hardy nursery stock	Vege-tables, bulbs	Cereal	Other arable	Grass	Orchard	Hops	Total agric, hort
	1980	1981/2	1981	1981/2	1982	1982	1982	1983	1983	1980-83
Organochlorines	16576	2093	2592	32350	9153	85858	128	6091	5382	160223
Contact organophosphates	5397	2606	2244	89092	56577	80234	723	27093	1848	265814
Systemic organophosphates	9366	2105	6670	164401	315898	123534	1197	29108	5378	657657
Carbamates	2616	3253	1504	38931	550443	295635	2181	23766	1987	920316
Pyrethroids	1907	3069	1700	25130	74901	3665	0	33972	27502	171846
Other ins/acar/moll	5351	2653	1021	172	78406	9485	4914	33333	681	136016
Total : ins/acar/moll	41213	15779	15731	350076	1085378	598411	9143	153363	42778	2311872
Total seed treatments	0	9	0	124254	3189459	565193	4441	0	0	3883356
Total ins/fung mixtures	0	264	28	0	0	0	0	0	0	292
Systemic fungs	23496	4416	9184	26359	4702753	105382	19412	157743	32128	5080873
Systemic/dithio.	53	1301	525	5798	252026	170694	2007	22	335	432761
Powdery mildew fungs	5802	811	6311	17	1890	0	0	78739	8874	102444
Dithiocarbamates	8576	3728	1909	13757	149805	233218	3004	4473	7555	426025
General fungicides	34705	10245	2950	13417	128309	55560	0	162645	2358	410189
Elemental fungs	3066	194	282	3080	11969	220322	0	14840	9185	262938
Total : fungicides	75698	20695	21161	62428	5246752	785176	24423	418462	60435	6715230
Total : herbicides	41274	850	19610	334100	7395138	1672082	2788256	127556	23390	12402256
Growth regulators	2	797	358	3456	770173	11433	0	8910	144	795273
Soil sterilants,disinfectants	70	2308	221	200	0	3122	0	0	3	5924
Total : other chemicals	72	3105	579	3656	770173	14555	0	8910	147	801197
Total treated area	158257	40702	57109	874514	17686900	3635417	2826263	708291	126750	26114203
Area grown	15105	4447	6003	194923	3444486	661287	6143427	35443	5912	10511033

TABLE 13 Total annual usage of pesticides 1980-83 - tonnes of active ingredients (Sly, 1985)

Chemicals	Soft fruit 1980	Pro-tected crops 1981/2	Hardy nursery stock 1981	Vege tables, bulbs 1981/2	Cereal 1982	Other arable 1982	Grass 1982	Orchard 1983	Hops 1983	Total agric, hort. 1980-83
Organochlorines	15.59	1.76	3.10	30.09	12.86	55.82	0.04	5.91	5.32	130.49
Contact organophosphates	4.70	15.37	2.62	134.08	48.87	43.68	0.54	21.23	1.40	272.49
Systemic	4.83	1.22	3.32	107.62	102.42	64.88	0.41	17.30	16.78	318.78
Carbamates	1.43	3.06	1.03	33.61	115.65	271.95	0.48	15.66	1.08	443.95
Pyrethroids	0.13	0.92	0.08	0.84	3.29	0.15	0.00	1.42	0.74	7.57
Other ins/aca/moll	20.76	5.91	2.19	0.16	70.57	5.94	4.42	110.34	0.44	220.73
Total ins/acar/moll	47.44	28.24	12.34	306.40	353.66	442.42	5.89	171.86	25.76	1394.01
Total : seed treatments	0.00	0.00	0.00	32.94	234.95	33.04	0.07	0.00	0.00	301.00
Total ins.fung mixture	0.00	3.44	0.03	0.00	0.00	0.00	0.00	0.00	0.00	3.47
Systemic fungs	9.55	6.29	4.57	12.42	1459.17	35.35	5.69	38.81	14.81	1586.66
Systemic/dithio.	0.04	1.16	0.79	6.52	511.99	194.64	2.16	0.02	0.29	717.61
Powdery mildew fungs	5.62	0.65	4.95	0.00	1.06	0.00	0.00	101.95	3.72	117.95
Dithiocarbamates	19.95	11.52	5.21	22.34	207.43	332.83	9.37	11.61	19.79	640.05
General fungicides	59.74	56.80	4.69	13.88	162.53	50.43	0.00	234.86	4.63	587.56
Elemental fungs	8.30	1.74	0.61	2.20	57.45	529.69	0.00	53.65	37.19	690.83
Total : fungicides	103.20	78.16	20.82	57.36	2399.63	1142.94	17.22	440.90	80.43	4340.66
Total : herbicides	68.84	2.10	33.03	743.25	12626.95	11653.54	974.27	180.71	77.50	26360.12
Growth regulators	0.00	0.33	0.18	12.20	1093.94	15.33	0.00	6.38	0.04	1128.40
Soil sterilants,disinfectants	25.39	452.56	76.94	7.82	0.00	1447.02	0.00	0.00	0.15	2009.88
Total other chemicals	25.39	452.89	77.12	20.02	1093.94	1462.35	0.00	6.38	0.19	3138.28
Total tonnes	244.87	564.83	143.34	1159.97	16709.12	14734.29	997.45	799.85	183.88	35537.52

these cause severe water quality problems because of their very slow degradation rates.

DDT is undoubtedly the most famous and infamous of the organochlorines. The U.S.E.P.A. cancelled all uses of DDT in 1973 (Ware, 1983) and the DOE has encouraged its demise in recent years due to its long term persistence in soils and its accumulation in food chains. The chemical structure for DDT is presented below:

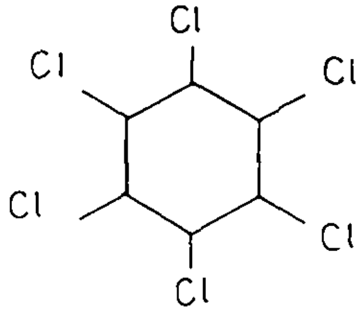


The chemical is highly persistent due to its chemical stability. Second, DDT's solubility in water is only about 6 ppb of water, i.e. probably the most water-insoluble compound ever synthesized. However, it is quite soluble in fatty tissue, and, as a consequence of its resistance to metabolism, it is readily stored in the fatty tissue of any animal ingesting DDT alone or DDT dissolved in the food it eats, even when it is part of another animal.-

HCH (Hexachlorocyclohexane)

HCH is made by chlorinating benzene, which results in a product made up of several isomers, that is, molecules containing the same kinds and number of atoms but differing in the internal arrangement of those atoms. HCH has five isomers, alpha, beta, gamma, delta and epsilon. But, only the gamma isomer has insecticidal properties. Since the gamma isomer is the only active ingredient, methods were developed to manufacture lindane, a product containing 99 percent gamma isomer, which is effective against most insects, but also quite expensive, making it impractical for crop use.

The structure of HCH is given below:

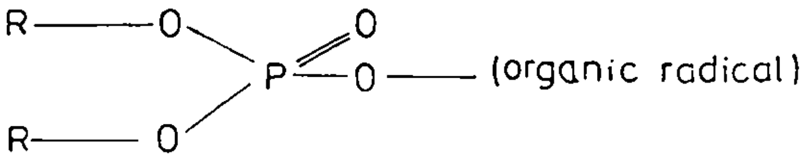


Cyclodienes

Generally, the cyclodienes are persistent and are stable in soil and relatively stable to the ultraviolet action of sunlight. Consequently, they have been used in greatest quantity as soil insecticides (especially chlordane, heptachlor, aldrin and dieldrin). Because of their persistence, their use on crops was restricted; undesirable residues remaining beyond the time for harvest (Ware, 1983). Most agricultural uses of these were cancelled by the EPA between 1975 and 1980, and their use has since been discouraged in the U.K. due to their persistence. Also, the cyvlodienes are highly toxic to fish (Ware, 1983) because when they are introduced into water the fish continually respire and ingest any toxic compound contained in their aquatic environment.

(ii) Organophosphates

The chemically unstable organophosphate (OP) insecticides have virtually replaced the persistent organochlorine compounds, especially in home and garden usage. As the name implies, these compounds are organically complexed phosphorous molecules which generally have the structure shown below:



These compounds are normally easily hydrolized and are therefore somewhat easily degraded. However, almost all of the compounds in this group have a very high toxicity in mammals.

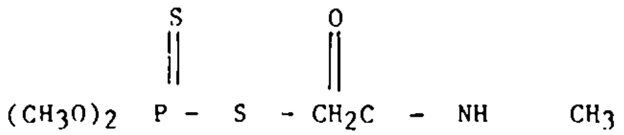
Thus the OPs have two distinctive features. First, they are generally much more toxic to vertebrates than are the OCs, and, second, they are chemically unstable or non persistent. They are divided into three groups - the aliphatic, phenyl, and heterocyclic derivatives.

Aliphatic Derivatives

The term aliphatic means "carbon chain" and the linear arrangement of carbon atoms differentiate them from ring or cyclic structures. All of these are simple phosphoric acid derivatives bearing short carbon chains.

Contained among the aliphatic derivatives are several plant systemics including the commonly used dimethoate shown below:

DIMETHOATE (Cygon)



$$(CH_3O)_2\overset{S}{\overset{\|}{P}} - S - CH_2\overset{O}{\overset{\|}{C}} - NH \quad CH_3$$

Systemic insecticides are those that are taken into the roots of plants and translocated to the above ground parts, where they are toxic to any sucking insects feeding on the plant juices.

Phenyl Derivatives

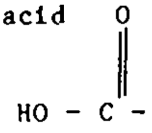
When the benzene ring is attached to other groups it is referred to as phenyl. The phenyl OPs contain a benzene ring with one of the ring hydrogens displaced by attachment to the phosphorous moiety and others frequently displaced by Cl, NO_2, CH_3, CN or S. The phenyl OPs are generally more stable than the aliphatic OPs; consequently their residues are longer lasting.

Heterocyclic Derivatives

The term heterocyclic means that the ring structures are composed of different or unlike atoms. In a heterocyclic compound, for example, one or more of the carbon atoms is displaced by oxygen, nitrogen or sulphur, and the ring may have three, five or six atoms. Generally they have longer-lasting residues than many of the aliphatic or phenyl derivatives. Also, because of the complexity of their molecular structures, their breakdown products (metabolites) are frequently many, making their residues sometimes difficult to measure in the laboratory.

(iii) Carbamates

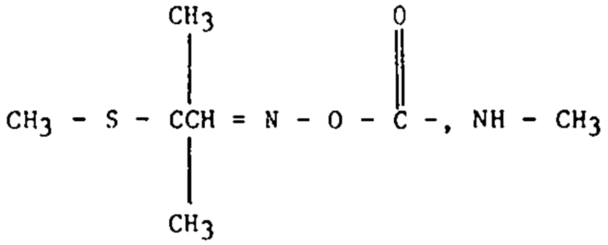
Carbamates are derivatives of carbonic acid



$HO - \overset{O}{\overset{\|}{C}} - NH_2$

and are broad-spectrum in effectiveness. Several of the carbamates are plant systemics, indicating that they have a high water solubility, which allows them to be taken into the roots or leaves. They are also not readily metabolized by the plants. For example, aldicarb, (shown below has distinct systemic characteristics.

ALDICARB (Temik)

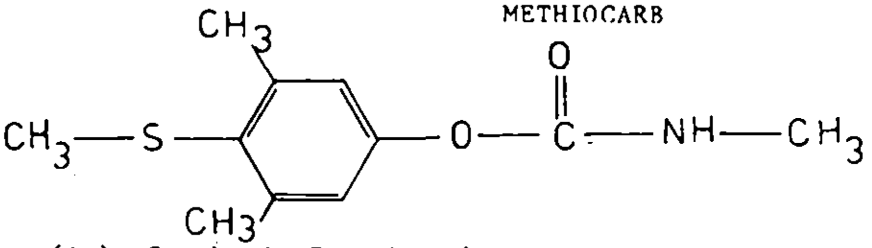


$CH_3 - S - \overset{CH_3}{\underset{CH_3}{C}}CH = N - O - \overset{O}{\overset{\|}{C}} -, NH - CH_3$

Aldicarb is also used as a soil insecticide and under rare circumstances has been detected in shallow groundwater following certain uses (Ware, 1983).

Methiocarb is another commonly used carbamate (shown below) and is effective against foliage- and fruit- eating insects, as well as against molluscs. It is also registered as a bird repellant for cherries and as a seed dressing.

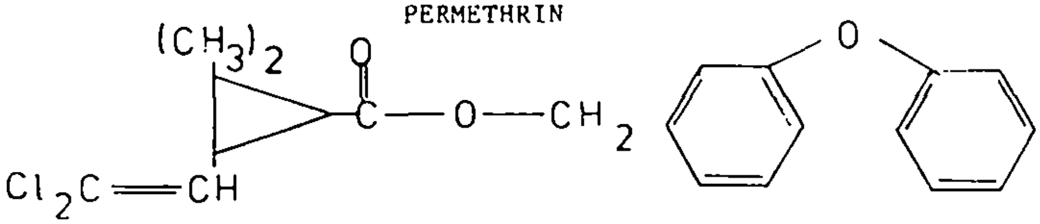
METHIOCARB



(iv) Synthetic Pyrethroids

These are very stable in sunlight and are generally effective against most agricultural pests when used at a low rate of 0.11 to 0.23 kg/ha. Examples are permethrin and decamethin. Permethrin (shown below) appeared in 1973:

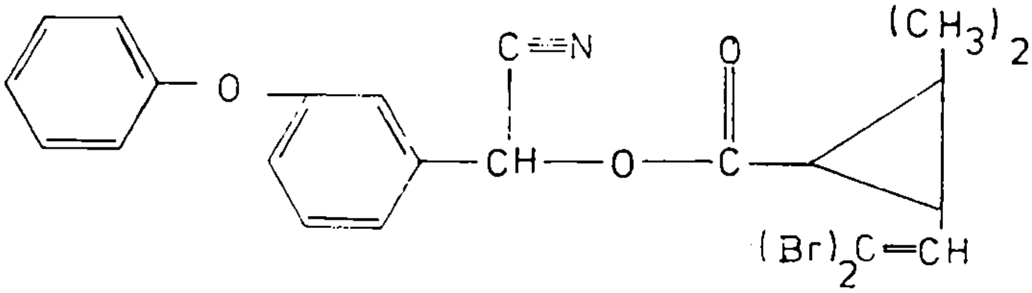
PERMETHRIN



One of the first agricultural pyrethroids because of its exceptional insectidal activity (0.11 kg AI/ha) and its photostability, lasting four to seven days on crop foliage as effective residues.

A more recent generation of pyrethoids, includes decamethrin, with rates of application reduced to one-tenth of the above (i.e. 0.01 to 0.06 kg AI/ha). This is fairly phenomenal compared to the rate of 1.1 to 2.3 kg AI/ha required of the OP, carbamate and OC insecticides. Decamethrin, is shown below:

DECAMETHRIN (Decis)



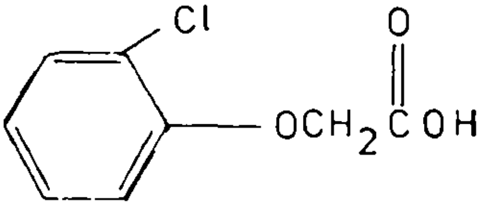
All of these insecticides are photostable, providing long residual effectiveness in the field at low applications.

b) <u>Organic Herbicides</u>

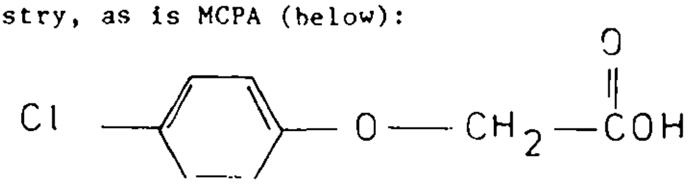
(i) Phenoxyaliphatic Acids

An organic herbicide introduced in 1944, later to be known as 2,4-D, was the first of these herbicides. These are highly selective for broad leaf weeds and are translocated throughout the plant. Several compounds belong to this group, of which 2,4-D, MCPA and the notorious 2,4,5-T are the most familiar.

All three of the above have been used for years in very large volume worldwide with no adverse effects on human or animal health. 2,4-D (shown below)



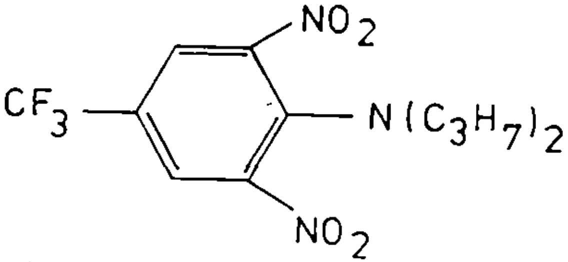
continues to be extremely useful. In agriculture it is used on cereal and grain crops for the control of broad-leaf weeds and on paths and in forestry, as is MCPA (below):



(ii) Nitroanilines

These are probably the most heavily used group of herbicides in agriculture. They are used almost exclusively as soil-incorporated pre-emergence selective herbicide in many field crops. A commonly used example in the U.K. is Trifluralin (shown below):

TRIFLURALIN (Treflan)



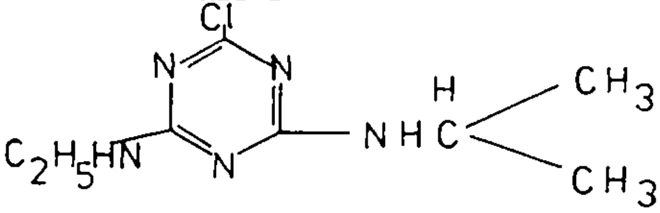
This has a very low water solubility which minimizes leaching and movement from the target.

(iii) Heterocyclic Nitrogens

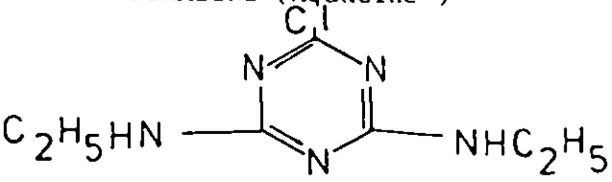
The triazines, which are six-member rings containing three nitrogens, and azine (a nitrogen containing ring) make up this group.

Probably the most familiar group of heterocyclic nitrogens, because of their heavy use are the triazines, which are strong inhibitors of photosynthesis. Their selectivity depends on the ability of tolerant plants to degrade or metabolize the parent compound (the susceptible plants do not). Triazines are applied to the soil primarily for their post-emergence activity. Two common ones are illustrated below:

ATRAZINE



SIMAZINE (Aquazine)

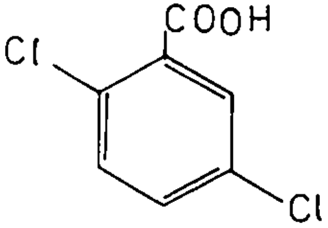


They are used in greatest quantity in corn production and nonselectively on industrial sites.

(iv) Aryaliphatic Acids

These are aryls, or six-member rings attached to aliphatic acids. For example, dicamba (below) is applied to the soil against germinating seeds and seedlings.

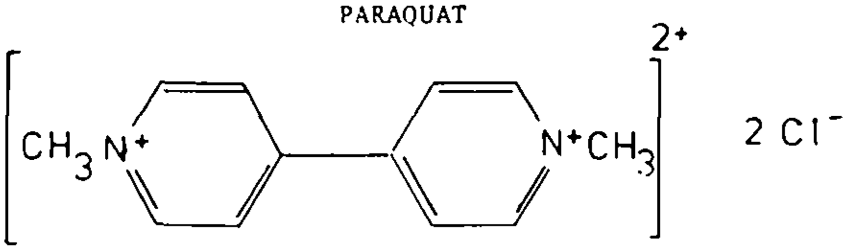
DICAMBA



(v) Bipyridyliums

There are two important herbicides in this group, diquat and paraquat. Both are contact herbicides that damage plant tissues quickly. Rapid wilting and dessication occur within hours. Neither is active in soils and in the U.S. they are only available to professional weed control specialists (Ware, 1983). Paraquat is more commonly used in the U.K. (Sly, 1985) and is shown below:

PARAQUAT

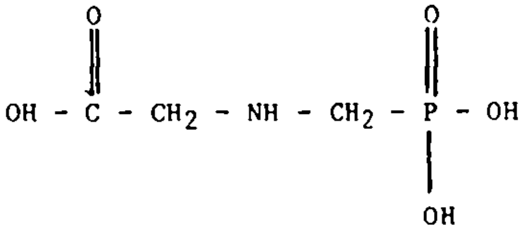


Because all the leaves drop off, paraquat is considered a defoliant and is often used on cotton, potatoes and soy beans.

(vi) Miscellaneous Herbicides

One such common herbicide used in the U.K. is Glyphosate, discovered in 1971. It is a nonselective, non residual, post-emergence material. It is recognised for its effectiveness against perennial, deep-rooted grass and broad-leaf weeds, as well as woody brush problems in crop and non crop areas. It is a translocated, foliar applied herbicide that can be applied at any stage of plant growth or at any time of year, with most types of application equipment. Its chemical composition is shown below:

GLYPHOSATE (Roundup)



$$HO-\overset{O}{\overset{\|}{C}}-CH_2-NH-CH_2-\overset{O}{\overset{\|}{\underset{OH}{\underset{|}{P}}}}-OH$$

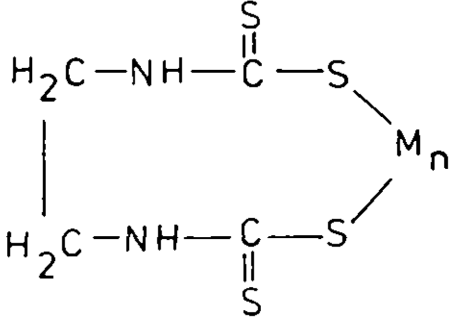
c) <u>Organic Fungicides and Bactericides</u>

The newer organic fungicides possess several outstanding qualities. They are extremely efficient - that is, smaller quantities are required than those used in the past; they usually last longer; and they are safer for crops, animals, and the environment. Most of the newer ones also have very low phytotoxicity and most are readily degraded by soil microorganisms, thus preventing their accumulation in soils.

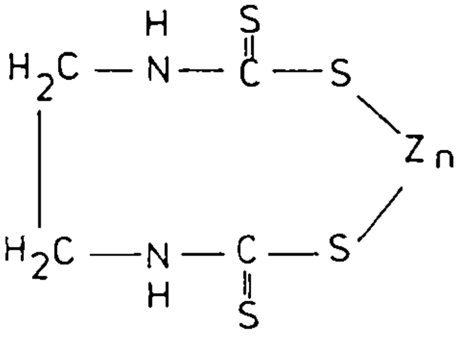
(i) Dithiocarbamates

Among these maneb and zineb shown below, were developed in the early 1940's.

MANEB



ZINEB

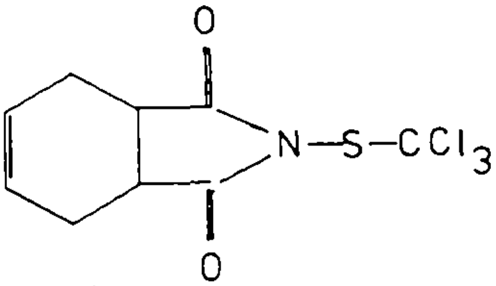


Such fungicides probably have greater popularity and use than all other fungicides combined. Except for systemic action, they are employed collectively in every use known for fungicides.

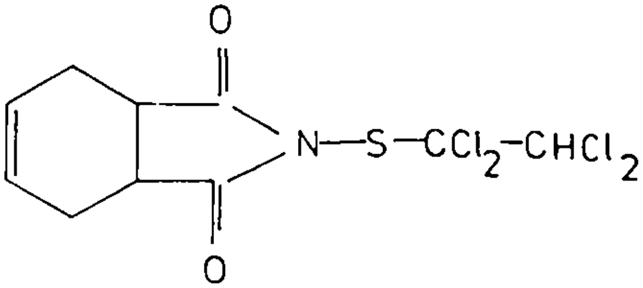
(ii) Dicarboximides

These are foliant protectant fungicides. Captan appeared in 1949 and is undoubtedly the most heavily used fungicide around the home of all classes and captafol appeared in 1961. They are both used primarily as foliage dusts and sprays on fruits, vegetables and ornamentals and are shown below:

CAPTAN



CAPTAFOL (Difolaton)



These are some of the safest of all pesticides available and are recommended for lawn and garden use, as seed treatments, and as protectants for mildews etc.

(iii) Systemic fungicides

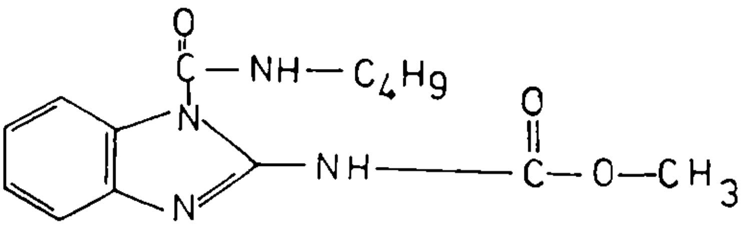
Only in recent years have successful systemic fungicides been marketed. Most have eradicant properties that stop the progress of existing infections. A few can be applied as soil treatments and are slowly absorbed through the roots to give prolonged disease control.

Systemics also reduce the risk of contaminating the environment by fraequent broad fungicidal treatments. Undoubtedly these will gradually replace the protectants that compose the bulk of the fungicides used at present.

(iv) Benzimidazoles

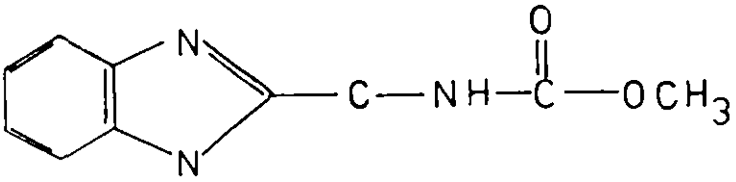
These are commonly represented in the UK by benomyl which was introduced in 1968 and is used against a broad spectrum of diseases. Benomyl (shown below) has the widest spectrum of fungitoxic activity of all the newer systemics.

BENOMYL



Also, carbendazim, introduced in 1973 has proved useful in controlling Dutch elm disease, when injected into tree trunks.

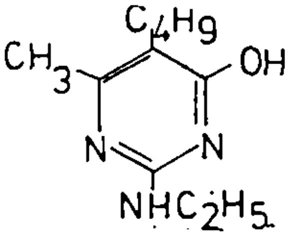
CARBENDAZIM (Lignason)



Pyrimidines

These systemic fungicides appeared in the late 1960s and include ethirimol (shown below):

ETHIRIMOL (Milcurb Super)

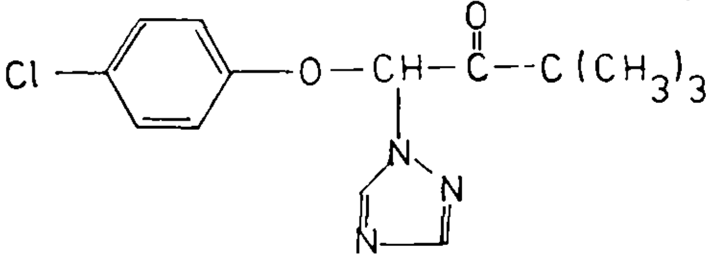


It is very active against specific types of powdery mildews, especially for cereals.

Traizoles

Lastly, Triadimefon is the sole systemic fungicide of the triazole group. It carries both protective and curative actions, and is effective against mildews and rusts on vegetables, cereals, deciduous fruit, grapes and ornamentals.

TRIADIMEFON (Bayleton)



1.4 Pesticide applications techniques

Pesticides are normally marketed as formulated products, ready for use directly or after dilution with water, or some other solvent. The majority of formulations are designed for use as sprays, other types include baits, dusts and granules.

The aim in application is clearly to use a pesticide as economically as possible to achieve the desired result, with minimum harm to the neighbouring environment. However, if a crop is sprayed from the air in high winds, for example, it will drift and may adversely affect people or livestock, and may destroy plants or hedgerows. Even ground spraying can be so badly done as to cause damage. Various application methods are thus commonly employed in the U.K.

a) Aerial Spraying

There has been an appreciable increase in aerial spraying in recent years (Sly, 1981), as shown below:

Aerial applications (,000 hectares)

Aircraft	1976	1977	1978	1979
Fixed Wing	413	405	339	393
Helicopter	137	177	247	259
Total	550	581	585	653

The above data also includes aerial applications of fertilisers and seed. However, despite this, an indication of the increase is still apparent. The most extensive usage was on cereals, potatoes, peas, beans and oilseed rape. Demeton-S-methyl, triazophos, dimethoate and pirimicarb were the most used insecticides while maneb, fentin acetate/maneb, triadimephon, carbendazim/maneb and tridemorph were the most used fungicides. Application of herbicides and other pesticides from the air accounted for only about four per cent of all applications (Sly, 1981).

It must be remembered that use of the more toxic or persistent chemicals is excluded and any special risks (such as that to bees) is carefully assessed.

Aerial spraying on forests is rarely practised in the UK, but during 1978 the Forestry Commission carried out a large scale operation on forests of lodgepole pine in the North of Scotland, spraying over 5000 hectares with the OP insecticide fenitrothion.

(b) Ultra Low Volume (ULV) and Controlled Droplet Application (CDA)

These techniques are largely associated with herbicides which account for nearly 75 per cent of the active ingredient used in agriculture in the

UK. With these methods, pesticides which are normally applied on farms in fairly diluted form by pumping them through nozzles to form a spray consisting of a mixture of large, medium and small droplets, at typical applications of 250 litres or more of spray mixture per hectare, with so called "low volume" applications ranging upwards of 100 litres/hectare, would be replaced by ULV methods, typically spreading about 25 litres/hectare in a more concentrated form. The associated CDA technique enables this more concentrated form to be projected from a spinning disc in droplets of a more uniform size. Thus, ULV/CDA techniques, if perfected, could lead to a reduction of up to 25 per cent in the total quantity of active ingredient used (DOE, 1979). However, extra precautions are necessary to avoid spray drift of these more concentrated sprays.

1.5 The Risks of Pesticide Use

Two properties of pesticides are particularly relevant to a consideration of their impact on the environment : these are their selectivity and persistence.

(a) Selectivity

Many modern pesticides are selective to a greater or lesser extent; that is, they are more toxic to some groups of organisms than to others. The selectivity may be increased by the choice of formulation or by the method and timing of application. However, in recent years due to the high cost of pesticide development, manufacturers have tended to look for chemicals which control a range of pests and diseases.

(b) Persistence

The rate of breakdown of an organic pesticide is dependent on its chemical structure and a wide variety of processes, which are affected by such factors as the soil type and acidity, temperature and moisture conditions. There is a wide range in the times of degradation, as shown in Table 14 below.

Table 14: Relative Persistence of some Major Pesticides Classes

CHEMICAL CLASS	USE	PERSISTENCE
OCs	Insecticides	2-5 years
Ureas	Herbicides	4-10 months
Triazines	Herbicides	3-19 months
Phenoxy	Herbicides	1-15 months
Carbamate	Herbicides, fumigates, insecticides	2-8 weeks
Aliphatic acids	Herbicides	3-10 weeks
OPs	Insecticides	7-84 days

Most of the OC insecticides are highly persisent, ie. they exhibit a very low rate of degradation. The OPs in contrast, persist only for a few days or weeks. It may also be noted however, that with the change to less persistent materials, the active ingredients of insecticides have tended to be more acutely toxic to man and other vetebrates. Although clearly while any such risks are highly localised in their extent, a reduction in spray drifting becomes increasingly important.

Moreover, it is insufficient to consider only the risks to the environment of the chemicals as applied, since some of the metabolic products they give rise to may be more damaging and even more stable than the original compounds, thus causing greater residue problems. For an example, the reader is referred to the work of Pleiva and Gentile (1976) on the herbicide atrazine.

In addition, there remains particular concern about the possible long term effects of the persistent OC compounds such as DDT, aldrin and dieldrin. Because of their early widespread use and their great persistence they have become widely dispersed in the environment and they constitute still the most prevalent and predominant of all pesticide residues in man, entering via the food chain.

1.6 Pesticide Residues in Soil and Water

It is clear that the distribution and fate of pesticides are determined by a host of variables that includes the nature of the pesticide and the many factors that determine the environment in which it is found (McEwen and Stephenson, 1979). Figure 2 depicts some of these factors.

(a) Pesticides in Soil

(i) Sources

Intentional Application

Direct application to the soil surface, incorporation in the top few inches, or application to crops are the routes by which most high concentrations of pesticides reach soil.

Unintentional Application

Large amounts also reach the soil through drift during application and through atmospheric fallout. For example, as much as 50% or more may be lost to the target area during aerial spraying due to variations in wind speed, droplet size and air temperatures. Also, with regard to atmospheric fallout, studies in the 1960's have demonstrated the presence of pesticides in rainwater and/or snow (Table 15).

Table 15 : Pesticides in Rainwater - some highest levels reported

PESTICIDE	AREA	LEVEL (ng/ℓ)	STUDY
DDT	England	[illegible]	Wheatley and Hardman (1965)
DDT	England	470	Abbott et al (1965)
DDT	England	46	Tarrant and Tatton (1968)
Dieldrin	England	40	Tarrant and Tatton (1968)
Dieldrin	England	95	Abbot et al (1965)
BHC	England	175	Abbott et al (1965)
BHC	England	260	Tarrant and Tatton (1968)

Source: Adapted from McEwen and Stephenson (1979)

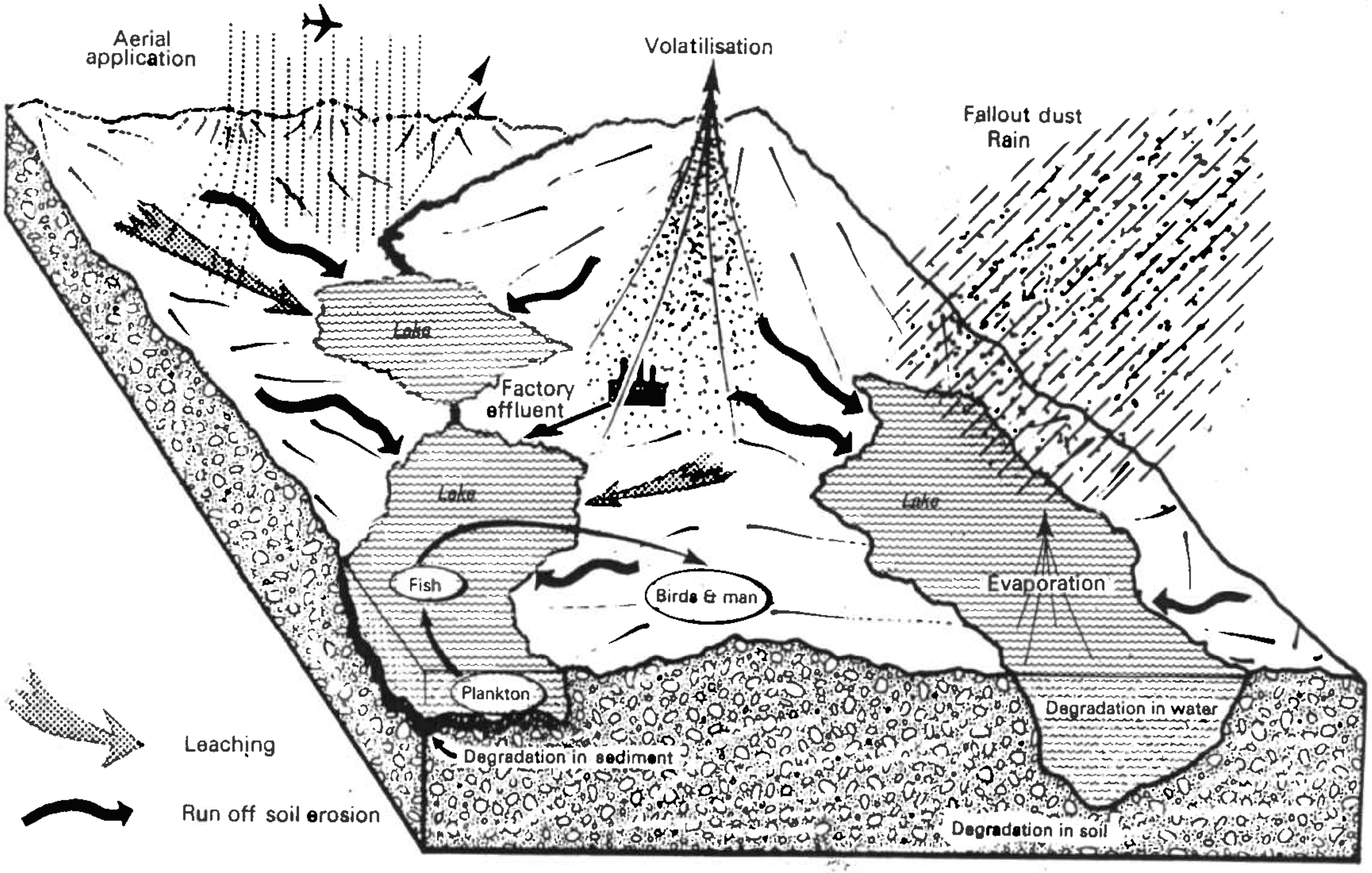


Figure 2. Pesticides in the environment and some factors important in their fate.

Seasonal use patterns generally suggest an explanation for some of the variations observed in the above studies, but not all. However, it is doubtful that the levels present in rainwater are sufficiently high to constitute a major source of soil contamination (Edwards, 1973).

(ii) Fate of Pesticides in Soil

Many factors influence the behaviour and fate of pesticides after contact with soil (Figure 3). These include (1) adsorption to clay and organic matter, (2) leaching with the downward percolation of water, (3) volatilisation to the atmosphere, (4) uptake by soil organisms or plants, movement with runoff water or eroded soil, (6) microbial degration, (7) chemical degradation, and (8) photolysis of primary importance is the chemical nature of the pesticide and the soil type. Environmentally the processes of adsorption and desorption are crucial since they influence most of the other processes determining the eventual fate of a pesticide.

Adsorption

Pesticides have varying tendencies to be adsorbed or attracted to clay or organic matter particles or to be dissolved in the soil solution. For the most part the adsorption sites on clay or organic matter are negatively charged and constitute the "Cation Exchange Capacity" of a particular soil. For each pesticide, soil type, and set of soil conditions, a different equilibrium is established between the amount adsorbed and the amount dissolved in the soil solution.

Soil Type

Of special importance are the soils clay and organic matter content, for these are colloidal and have a high cation exchange capacity and surface area. Thus, higher rates of pesticide application are required for effective control if soils are high in either clay or organic matter, since in such soils, much of the pesticide is adsorbed and not active, therefore producing more persistent residues.

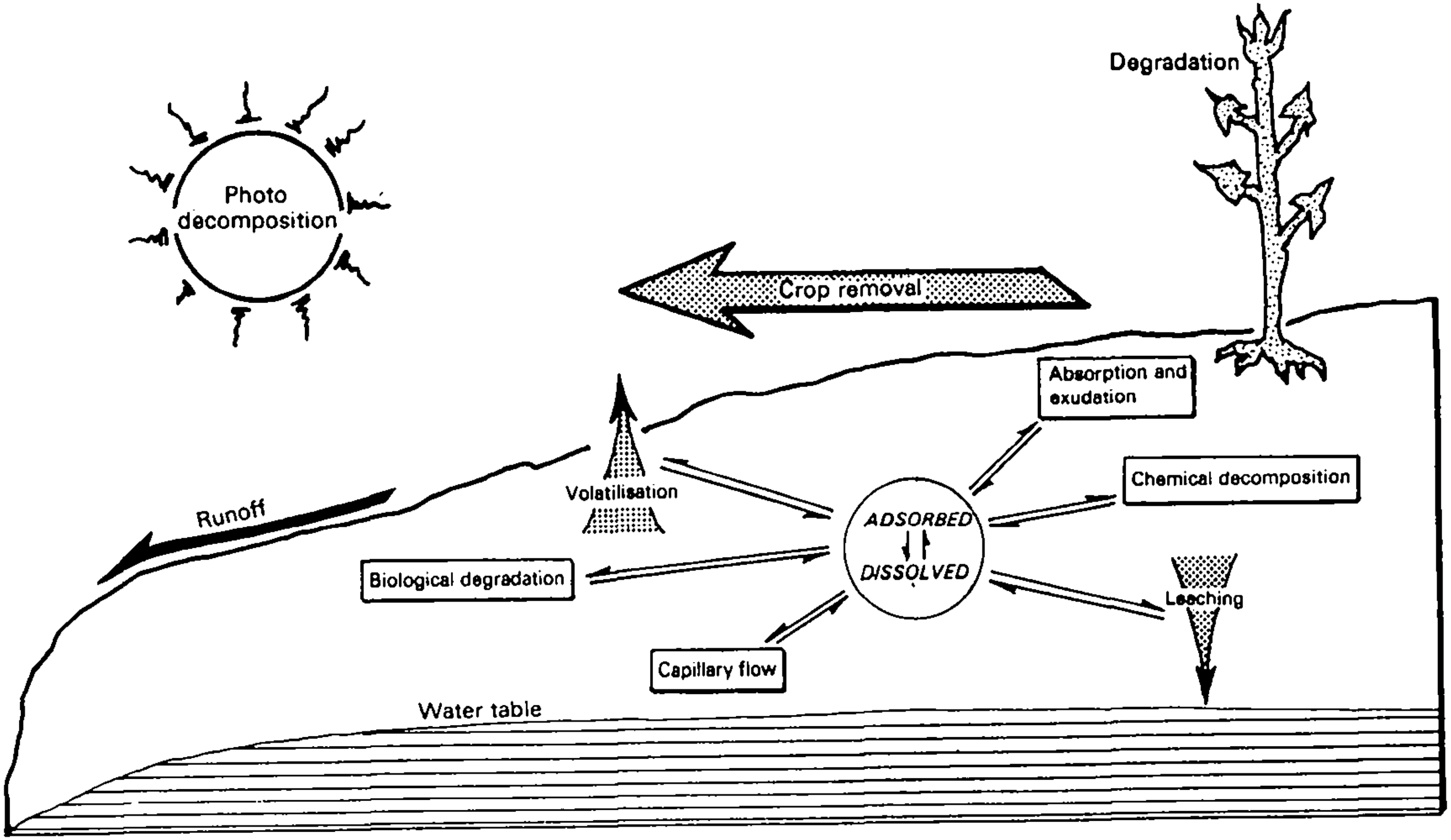


Figure 3. Processes influencing the behaviour and fate of pesticides in the soil environment (redrawn and modified from Weber et al., 1973).

Nature of the Pesticide

The chemical structure of a pesticide determines sorption equilibrium by influencing its direct affinity for the clay or organic matter, or by influencing its solubility or affinity for the soil solution. Many investigators have noted a general but not precise inverse correlation between pesticide solubility and adsorption (McEwen and Stephenson, 1979). Also, granular formulations are usually the most persistent. Wettable powder and dust are often less persistent than emulsifiable preparations.

Soil Moisture Content

One would expect more pesticide to be adsorbed in dry soils. This is true in moderately light to very light soils, but not in heavy soils, however (McEwen and Stephenson, 1979). Thus, because water molecules are themselves polar they begin to compete with the pesticide molecules for adsorption sites on the soil colloids, forcing more of the pesticide into solution.

Soil pH

The fate of pesticides in soil varies with pH, primarily because of the influence of pH on sorption. Soil pH also affects chemical degradation and thus pesticide adsorption is usually highest in more acid soils. However, within normal pH ranges, slight increases in acidity may convert pesticides from negatively charged anions to uncharged molecules or even to positively charged cations, and thus dramatically increase their sorption. But, when soils are extremly acid, most of the cation exchange sites are occupied by hydrogen cations, and pesticide adsorption is consequently low due to the lack of negative sites. Adsorption is also very low at extremely high pHs.

Soil Temperature

Pesticide adsorption in soil is an exothermic process. When hydrogen or ionic bonds are formed, heat is given off. Thus, when the soil temperature increases, the input of heat can break some of these bonds and cause desorption of some pesticide molecules.

Leaching

Solubility is an important aspect related to pesticide persistence in soil. Within limits, pesticides highly or moderately soluble in water are leached from soils more quickly than those that are less soluble.

Movement with Runoff water

As water moves laterally over a sloping soil surface, pesticides can be described and moved with runoff. Lateral movement is likely to be greatest under conditions of least adsorption.

Movement with Eroded Soil

No soil applied pesticide is immune to transport if it is adsorbed onto soil particles. The longer it remains adsorbed at or near the soil surface without degration, the more likely it is to be eroded.

Volatilization

Several factors influence pesticide volatilization. The structure of the chemical is important since it determines its vapour pressure. Cool, dry conditions in soils with high organic matter or clay content, normally result in very little loss of even the most volatile chemicals, since they are adsorbed tightly. Conversely, warm, moist conditions give greater desorption and greater volatilization losses.

Microbial Degradation

The primary microorganisms in soil are algae, fungi, actinomycetes, and bacteria. Most of these are dependent on organic compounds for energy and growth. When an organic pesticide is added to soil and reaches an equilibrium between the soil colloids and the soil solution, any molecules in the soil solution are immediately attacked as potential energy sources.

Thus, any factors that encourage the growth of degrading microorganisms or that increase the availability of the pesticide in the soil solution will enhance the disappearance of the chemical. Thus, conditions such as warm temperatures, adequate soil moisture and aeration, unextreme pH, and adequate fertility, encourage microorganisms and increase desorption and the availability of pesticides.

Chemical degradation

Chemical reactions in soil can destroy the activity of some pesticides and activate others. Whereas adsorption normally decreases microbial degradation rates, it may enhance the chemical degradation of some compounds. In chemical degradation pH is important, but its exact influence varies for different pesticides. For example, the herbicide atrazine degrades faster at a low pH (Armstrong and Chesters, 1968), whereas malathion breaks down quicker at a high pH.

Photodegradation

Few organic pesticides are completely resistant to photolysis, but it is probably not a major means of pesticide inactiviation or disappearance in soil.

(iii) Conclusion

It is clear that there are many different processes that influence the movement, persistence and activity of pesticides in the soil. It is also clear that there are countless ways in which these processes can interact, as seen in Figure 4.

However, with few exceptions, the only pesticide residues reported in soil surveys have been either persistent inorganic chemicals such as arsenic, that were used as insecticides prior to 1945, or persistent O.C. insecticides (Edwards, 1973). Residues of very few OP insecticides have been reported from areas of intensive use. Unfortunately, little information exists for UK soils (Edwards, 1973).

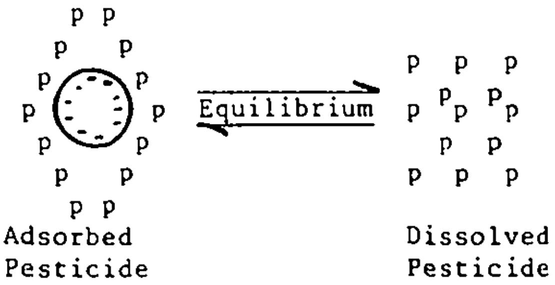
In almost all the UK soils surveyed the commonest chemical has been DDT, with the next most common being dieldrin. Few others have been found in UK soils as seen in Tables 16 and 17.

Factors resulting in greater desorption

1. Higher soil temperature.
2. Higher pesticide solubility within related groups.
3. Higher soil moisture content in light soils.
4. *Greater percent sand.*
5. Higher soil pH.

Adsorbed pesticides are more likely to:

1. Move with eroded soil.
2. Be taken up by earthworms if lipophilic.
3. Be degraded chemically.



Desorbed pesticides are more likely to:

1. Volatilize from the soil.
2. Move downwards by leaching.
3. Move laterally with run-off water.
4. Be degraded by microorganisms.
5. Be taken up by higher plants.

Factors resulting in greater adsorption:

1. Higher clay content.
2. Higher organic matter content.
3. Greater polarity of the pesticide molecule.
4. Cationic nature of the pesticide molecule.

Figure 4 Interrelationship of processes influencing the fate of pesticides in soil.

Table 16 Residues of DDT and related compounds in soil

Location	Reference	No. Sites	Crop	Residues in ppm Max	Residues in ppm Mean
Orchards & Vineyards					
G.B.	Edwards, 1969		Fruit	131.1	61.8
Agricultural					
G.B.	Wheatley et al, 1962	21	Potatoes	0.96	0.2
G.B.	Davis, 1968	10	Mixed	0.80	0.3

Source: Edwards (1973)

Table 17 Residues of other organochlorine insecticides in soil

Location	Reference	No. Sites	Crop	Residues in ppm Max	Residues in ppm Mean
Horticultural					
G.B.	Edwards, 1969		Carrots	1.47	0.68 (Dieldrin)
Agricultural					
G.B.	Wheatley et al, 1962	21	Potatoes	0.12	0.12 (Aldrin)
G.B.	Davis, 1968	10	Mixed	0.7	0.15 (Aldrin)
				0.7	0.15 (Dieldrin)
G.B.	Edwards, 1969		Cereal	0.5	N.A. (Y-BHC)

Source: Edwards (1973)

(b) Pesticides in water

The widespread use of pesticides makes it inevitable that a portion of these will contaminate surface waters (McEwen and Stephenson, 1979). Hence, water, and the mud at the bottom of rivers are major reservoirs for persistent residues.

(i) Sources

Waters are contaminated in the same way as soils through pesticide drift during application and as atmospheric fallout of rain and dust. Additionally, water may be contaminated through soil erosion, industrial effluent, sewage and occasionally by spills into, or adjacent to, water courses.

Atmospheric fallout

It is established that rain water contains pesticides. Some contamination also occurs by the settling of atmospheric dust. No precise data, however, exists.

Soil Erosion

Where pesticides are applied to land, those soluble in water may be carried to nearby waters by surface runoff, and either soluble or insoluble pesticides may be carried on soil particles in runoff or eroded by wind.

Industrial effluent

Many industries use pesticides in the manufacture of their products, and effluents may contain high levels. Many instances have been reported where DDT, lindane or dieldrin has been discharged from carpet or fabric manufacturing plants, where they are used for mothproofing.

Sewage

Pesticide sources in sewage include some discharges from industry, residues from homeowner's use, and a variety of fungicides and bactericides used in soaps and cosmetics. The level of contamination may be high. Edwards, (1973) cites instances where dilutions of 1:20 were required before effluents would be safe for fish. For some pesticides, for example, hexachlorophene, urban wastewaters probably represent the major source (Sims and Pfaender, 1975).

Spills

The handling of pesticides in the volumes now used increases the possibility of large-scale industrial spills during processing, storage and transportation, as well as the problem of smaller spills by individual applicators.

(ii) Fate of pesticides in water

The persistence of pesticides in water depends on a number of factors, only some of which can be qualified and/or quantified. Those that persist in soil also persist in water or in river sediments, from which mixing with the overlying water constantly occurs.

Nature of the pesticide

With organic pesticides those that are highly soluble are hydrolyzed rapidly and have a short life in water. Among the pesticides, DDT, dieldrin and endrin are the most persistent, as each are relatively insoluble in water (o.2 ppb, 186 ppb and 100 ppb, respectively) and resistant to hydrolysis. Hence, these have the potential to persist in rivers and river sediments. For most pesticides however, persistence in water is brief, irrespective of their solubility.

Nature of the Water

The natural composition of the water also plays an important role in the fate of pesticides in water.

Chemical composition

Some studies have considered water hardness (as $CaCO_3$) as important. However while some indicate that hardness is important in determining toxic effects, others indicate that it has little effect on persistence and toxicity (McEwen and Stephenson, 1979).

pH

Since many pesticides degrade by hydrolysis it might be assumed that water pH would be important. However, although laboratory findings make it clear that pH is important to degradation it may be of only minor significance in natural waters (McEwen and Stephenson, 1979).

Temperature

Increases in temperature increase the rate of chemical reaction and the rate of volatilization of pesticides. Within limits they will also increase biological activity and thus would be expected to increase biological degradation of pesticides.

Aquatic Life

Numerous studies attest to the fact that a wide range of plants and animals detoxify pesticides. Any consideration of the biota to which pesticides are exposed, must include that of the bottom mud, where anaerobic and near anaerobic conditions prevail. Some of the mechanisms involved in bilogical degradation include oxidations, dechlorinations, reductions, hydrolyses, and ring cleavage.

Of all the groups involved, microorgranisms are probably most important.

Sediment and Suspended Matter

Many studies indicate that bottom sediments in rivers act as reservoirs for persistent pesticides. Analysis of suspended matter demonstrates a tendency for pesticides to become adsorbed or absorbed to particulate matter whether organic or inorganic, living or dead.

(iii) Residue levels in surface waters

Estimates have been made of the "safe" level for pesticides in drinking water and Ettinger and Mount (1967) have noted the potential for fish to accumulate some pesticides, suggesting maximum levels in water which would give a reasonable measure of fish safety (Table 18). More recently, maximum permissible levels have been recommended to protect fish and aquatic life (Committee, 1973). These are much lower (see Table 18).

Also, a number of studies have correlated pesticide levels in streams with local use patterns and rainfall. Thus, Miles and Harris (1971) found that the highest levels of DDT in streams in an agricultural area reflected spring runoff and rainfall patterns throughout the growing season. Thus, sheet erosion probably constitutes a major source of contamination.

Many of the factors that determine persistence in soils apply to the problem in water. Table 19 gives a summary of the relative persistence of some pesticides in natural waters (McEwen and Stephenson, 1979).

In British rivers, only DDT, BHC, aldrin and dieldrin had been reported up to 1973. Up to then, only two surveys were available. The first was a study in 8 south east rivers and 18 rivers from other parts of the country (Croll, 1969). The amounts reported were relatively small, being generally less than 50 ng/ℓ, the occasional larges residues were attributed to industrial effluents (Table 20). There were no residues in the 12 different groundwater samples analysed.

TABLE 18 Levels of some pesticides permissible in potable water and safe levels for surface waters[a]

		Maxmimum Suggested	
Pesticide	Permissible Level[ab]	Fish[ac]	Aquatic Life[ab]
Dieldrin	1	0.25	0.005
Endrin	0.5	0.1	0.002
DDT	50	0.5	0.002
Heptachlor	0.1	1.0	0.01
Aldrin	1	0.25	0.01
Lindane	50	5.0	0.02
Chlordane	3	0.25	0.04
Methoxychlor	1000	20.0	0.005
Toxaphene	5	2.5	0.01
2,4-D	20	not given	--
2,4,5-TP(Silvex)	30	not given	--
2,4,5-T	2	not given	--
Organophosphorous plus carbamates	100	not given	--

[a] Level expressed as parts per billion.

[b] From Committee, 1973.

[c] From Ettinger and Mount, 1967

TABLE 19 **Relative persistence of some pesticides in natural waters**

Non Persistent[a]	Slightly Persistent[b]	Moderately Persistent[c]	Persistent[d]
azinphsmethyl	aldrin	aldicarb	benomyl
captan	amitrole	atrazine	dieldrin
carbaryl	CDAA	ametryne	endrin
chlorphyrifos	CDEC	bromacil	hexachlorobenzene
demeton	chloramben	carbofuran	heptachlor
dichlorvos	chlorpropham	carboxin	isodrin
dicrotophos	CIPC	chlordane	monocrotophos
diquat	dalapon	chlorfenvinphos	
DNOC	diazinon	chloroxuron	
endosulfan	dicamba	dichlorbenil	
endothal	disulfoton	dimenthoate	
fenitrothion	DNBP	diphenamid	
IPC	EPTC	diuron	
malathion	fenuron	ethion	
methiocarb	MCPA	fensulfothion	
methoprene	methoxychlor	fonofos	
methyl parathion	monuron	lindane	
mevinphos	phorate	linuron	
parathion	propham	prometone	
naled	Swep	propazine	
phosphamidon	TCA	quintozene	
propoxur	thionazin	simazine	
pyrethrum	vernolate	TBA	
rotenone		terbacil	
temephos		toxaphene	
TFM		trifluralin	
2,4-D			

[a] Half-life less than 2 weeks

[b] Half-life 2 weeks to 6 weeks

[c] Half-life 6 weeks to 6 months.

[d] Half-life more than 6 months

Source: McEwen and Stephenson (1979)

TABLE 20 Residues of organochlorine insectitudes in water

Location	Ref	No	Sites	BHC		Dieldrin		DDT R	
				Max	Min	Max	Min	Max	Min
GB	Croll, 1969	76	British rivers (2 monthly samples)	118.0	25.82	423	25.16		
GB	Croll 1969								
GB	Croll, 1969	15	British rivers (single samples)	214	53.64#	2840.0	291.64#	43^{+}	8.67
GB	Lowden et al, 1969	9	British rivers	98	18.7	40	3.3	15	1.6
GB	Lowden et al, 1969	9	Yorkshire rivers	180	38.6	630	114	908	64.6
GB	Lowden et al, 1969	21	Sewage effluents	390	92.5	1900	145	800	130.9
GB	Lowden et al, 1966		Sewage effluents			300	200	130	36

+ residue found at only one site

affected by a few large values

Source : Edwards (1973)

(c) Drinking Water Quality and Pesticides

The WHO guidelines for drinking water quality with regard to organic constituents are presented in Table 21. Many of these organic constituents are potentially toxic and can reach surface or groundwater either from point or non-point sources. Many too are carcinogenic and a number have been shown to be mutagenic.

In some cases where no threshold of toxicity exists, such as carbon tetrachloride multistage extrapolation models have been used to give an indication only, of potentially harmful levels to individuals and communities.

No reasonable person would dispute the immense usefulness, in terms of food production and health protection, of the wide range of pesticides now available to mankind. Equally, it would be absurd to suggest that these chemicals should be utilised without any controls designed to protect human beings and the ecosystem from harmful effects resulting from this use.

In water, the CEC Directive sets two maximum allowable concentrations for pesticides and related products, including insecticides, herbicides, fungicides, PCB and PCT (Table 22). These are:

a) for substances considered separately 100 ng/l
b) for all such substances, 500 ng/l

A comparison shows that, for the small number of pesticides and related compounds covered in the WHO guidelines the total concentration is 134 µg/l compared to only 0.5 µg/l (i.e. 500 ng/l) for all pesticides and related products allowed by the CEC Directive. Hence, one figure is 268 times the other. Clearly there is a danger that unenforceable or ill-considered controls could lead to disregard of the whole problem of pesticides in drinking water as will be seen later.

d) Some recent case studies of pesticide residues in river waters

(i) Pesticide Pollution in Australia

Garman and Sutherland (1983) have studied the extent of pesticides as non-point source pollutants in Australia. As in the U.K., herbicides

TABLE 21 WHO Guidelines for drinking water quality

Organic Constituents	
Substance	Guideline value (μg/l)
Aldrin and Dieldrin	0.03
Benzene	10
Benzo-a-pyrene	0.01
Carbon tetrachloride	3
Chlordane	0.3
Chlorobenzene	no guideline set
Chloroform	30
Chlorophenols	no guideline set
2:4D	100
DDT	1
1:2-Dichloroethane	10
1:1-Dichloroethane	0.3
Heptachlor and Heptachlor epoxide	0.1
Hexachlorobenzene	0.01
Gamma-HCH (Lindane)	3
Methoxychlor	30
Pentachlorophenol	10
Tetrachloroethane	10
Trichloroethene	30
2:4:6-Trichlorophenol	10
Trihalomethanes	no guidelines set

TABLE 22A EEC directige for drinking water quality Al.1 pesticides and related products (including PCBs)

	Directive level (μg/l)
For any one substance	0.1
For all substance together	0.5

22B WHO Guidelines for drinking water quality pesticides (only 8 categories covered)

	Guideline value (μg/l)
DDT	
Aldrin and Dieldrin	0.03
Chlordane	0.3
Hexaclorodbenzene	0.01
Heptachlor and Heptachlor Expoxide	0.01
Gamma HCH (Lindane)	3
Methoxyclor	30
2:4D	100
TOTAL	≅ 134

i.e. Total concentration suggested by WHO guidelines (for only 8 pesticides) is 268 times allowable concentration for all pesticides under EEC directive not suspected to cause problems of toxicity, taste etc. in potable waters, they do however, exceed the EEC "Drinking Water" Directive limits for pesticides.

1.8 Modelling Pesticides in the aquatic environment

Numerous investigators in the U.S. have developed models for assessing water pollution from nonpoint sources as indicated by Haith (1982). Bailey et al (1974) and Leonard et al (1979) have developed models which quantitatively describe pesticide runoff as a function of pesticide and soil properties, agricultural practices, watershed characteristics, and climatic factors. Unfortunately, as indicated by Dickinson and Wall (1977), many such models suffer from the following weaknesses: a) the components and parameters are of a conceptual rather than physical nature b) an inadequate characterization of the dynamic development of basin drainage systems c) no identification of the soil moisture storage concepts d) no description of micro-drainage systems, and e) insufficient emphasis on the role of large storms. In addition to these deficiences, most models: a) assume instantaneous equilibrium between adsorbed pesticides and those in solutions, b) assume completely reversible adsorption processes for all pesticides, c) apply uniform equations to all organic chemicals regardless of their chemical properties, d) assume that the diffusion and hydrodynamic dispersion of organic chemicals are insignificant, even for volatile chemicals, e) assume saturated flow conditions, and f) they do not include chemical decomposition and volatilization losses.

However, notwithstanding the above limitations, a brief review of some of the available pesticide models is presented in an effort to indicate the possibility of their successful development in the British context.

a) Agricultural Runoff Management (ARM) model (Donigan et al, 1977)

Skogerboe (1982) described the above model as a continuous one which simulates rainfall, sediment, pesticides and nutrient contributions to stream channels from both surface and subsurface sources. In this model, pesticide adsorption/desorption and degradation are modelled. In order to simulate vertical movement and transformations of pesticides and nutrients in the soil profile, specific soil zones (and depths) are established so that the total soil mass in each zone can be computed. Total soil mass is a necessary ingredient in the pesticide adsorption/desorption reactions and nutrient transformations. The vertical soil zones simulated in the ARM model include the surface, upper, lower and groundwater zones. The depths of the surface and upper soil zones are specified by the model input parameters, and are generally 2 - 8 mm and 75 - 150 mm, respectively. The upper zone depth corresponds to the depth of the incorporation of soil-incorporated chemicals.

The transport and vertical movement of pesticides and nutrients, as conceived in the ARM model, is indicated in Figure 5. Pollutant contributions to the stream can occur from the surface zone, the upper zone, and the groundwater zone. Surface runoff is the major transport mechanism carrying dissolved chemicals, pesticide particles, sediment, and adsorbed chemicals. The interflow component of runoff can transport dissolved pesticides or nutrients occurring in the upper zone. Vertical chemical movement is the result of infiltrating and percolating water. From all the zones, uptake and transformation of nutrients and degradation of pesticides is allowed. The groundwater zone is however, considered a sink for deep percolating chemicals.

b) Chemicals, Runoff and Erosion from Agricultural Management Systems: the CREAMS model.

Knisel (1982) has reported on the CREAMS model which also considers the effects of agricultural non-point source pollution and includes a consideration of pesticide modelling. The model was designed for field-size areas and was physically based, not requiring calibration. Also, input data requirements were restricted to readily available or easily measurable information. Thus, the adopted system for the evaluation of non-point source pollution in CREAMS, is shown in Figure 6. CREAMS is a state of the art field-scale model for evaluating response from alternative agricultural management practices. Also, the model can be used to develop resource conservation practices, however, it is not a predictive model in absolute quantities, but it provides estimates of the relative response among different management practices.

It has three major components (programs): hydrology, erosion, and chemistry. Each operates separately, and generates information to be used with the next component.

account for a large proportion (about half) of total sales, and OC pesticides use has given way to increasing use of OPs and Pyrethroids. The main mechanisms of transport were spray drift (as much as 75% loss from target areas depending on climatic conditions) and surface runoff. The types and amounts of pesticides transported in runoff depended on:

(1) Frequency and rates of application
(2) Application methods e.g. foliar, soil incorporation.
(3) The persistence, volatility and mobility of the compounds
(4) The intensity and duration of runoff events
(5) Elapsed time between applications and storm events.

The amounts of surface runoff inputs in agricultural lands were assessed for a range of catchments and agricultural land uses (Garman and Sutherland, 1983). Total exports of DDT, Dieldrin and Linuran ranged from 0.004% to 0.006%, 0.035 % to 0.31% and 0.02% to 0.03% respectively. The results of this AWRC study were thus consistent with, although generally much lower than, the working limits for losses suggested by Wauchope (1978) on the basis of U.S. studies:

(i) Average losses of 1% for foliage applied OC insecticides
(ii) Losses of 2% - 5% for wettable powder-formulated herbicides (e.g. atrazine and Limuran).
(iii) Losses of 0.5% for non OC insecticides, incorporated insecticides and all other herbicides.

Of course significantly higher losses may occur in particular circumstances such as an intensive storm immediately after treatment.

The effects of pesticide runoff on receiving waters were also investigated. Maximum concentrations of DDT were lower than the recommended drinking water limit (1 µg/l), except for storm runoff and drainage flows from some intensive agricultural areas. However DDT concentrations did exceed the criterion for the protection of aquatic life (0.001 µg/l) in about 10% of samples, by up to 3 times. Maximum concentration of dieldrin tended to be higher than for DDT, but below their drinking water limit (1 µg/l) except in storm flows from cultivated lands. Dieldrin was also detected in a significant percentage of samples (up to

50%). Mean concentrations exceeded the criterion for protection of aquatic life by up to 2 times.

(ii) Pesticide pollution in runoff in the U.S. and Canada

Weber, Shea and Strek (1980) have evaluated nonpoint sources of pesticide pollution in runoff in the U.S. Firstly, they evaluated the pesticide runoff found during seasonal or long-term studies. Generally, the loss of pesticides in runoff was found to be relatively low, averaging 2.39% for atrazine, 0.54% for Cyanazine, 1.33% for Simazine, 0.33% for 2,4-D, 1.08% for Carbofuran, 0.12% for Linuran, 0.36% for Toxaphene and 0.22% for Trifluralin, for example. The highest amount of runoff from any one pesticide was 15.9% of the total applied for atrazine. The next highest losses were 7.2, 6.1, 5.7, 5.7, 5.4, 5.4 and 5.1 percentages for diphenamid, propazine, terbuthylazine, atrazine, atrazine, simazine, and atrazine, respectively. Hence, the highest losses were from the wettable powder formulations, especially when they are applied to the soil surface. Higher losses also occurred from bare soil cover.

Secondly, maximum concentrations found during short-term runoff studies were evaluated. The maximum pesticide concentrations found in runoff sediment were 40, 30, 21.8, 13, 12, and 11 ppm for arsenic acid, terbuthylazine, propazine, fluometuron, dieldrin and atrazine, respectively. The highest concentrations found in the solution and sediment phase were 5.2, 4.8, 4.7, 4.2, and 4.2 ppm for picloram, dicamba, atrazine, 2,4-D salt, and picloram, respectively.

Numerous case studies of pesticide losses in individual catchments in North America also exist. For example, Nicholaichuk and Grover (1983) looked at the losses of 2,4-D applied to wheat in South Western Saskatchewan. The loss was greater from the treated stubble compared with fallow, which served as a control. Average losses were 4.1% of the amount applied and correlation analysis showed the amount of loss to be a function of runoff. Hence, a simple correlation of runoff volume and losses from an application rate of 0.42 kg/ha for the 6-year period resulted in the following equation:

$$Y = 0.45\ X - 2.3 \quad (r^2 = 0.96)$$

where Y = herbicide loss (g/ha), and X = runoff volume (mm). However, the average flow-weighted mean concentration of 31 μg/l was well below the USEPA maximum permissible level of 100 μg/l.

Finally, in the U.S., Wu, Correl and Remenapp (1983) have recently investigated herbicide losses in runoff from experimental watersheds in the Rhode River region of Maryland. Both atrazine and alachlor (herbices used in cornfields) were investigated. Although alachlor was applied in greater quantities, atrazine was detected more frequently in runoff waters and at greater concentrations than alachlor (0.40 μg/l vs 0.6 μg/l). Atrazine was also more persistent and more mobile in watershed soils. Lastly, a major portion of atrazine was found in dissolved aqueous form in runoff samples collected during storms, with percolation in subsurface flow and dissolution in overland flow believed to be the important transport mechanisms.

1.7 A U.K. Water Authority Perspective

Initial indications of the respective water authorities perspective of any pesticide pollution problem in the UK have been assessed based on their response to a letter sent from the authors. To date, the Welsh Water Authority has indicated the existence of localised problems in connection with sheep dipping and aerial spraying of bracken, (Buckley, pers comm, 1985). Severn Trent W.A. have also indicated the existence of some problems, especially in connection with herbicide usage. However, most detailed responses have arisen from meetings arranged with Thames, Yorkshire and Anglian water authorities.

(a) Thames W.A.

The major problem seems apparent rather than real and has been created by the blanket application of the EEC guidelines on drinking water, which calls for a maximum permissible concentration of 500 ng/l for total pesticides and 100 μg/l for individual pesticides, after treatment. In the case of the Thames W.A., concentrations of the herbicides simazine and atrazine in the river water used for supply, exceed the individual limits. The authority favours a change in the application of the limits, rather than treatment of its waters for compliance. In addition, the actual source of these two herbicides is unknown, although it is likely to be agricultural. However, other pesticide sources in the area include power station cooling waters treated with algacides and bactericides and paper mill discharges. Some concern about more localised pollution was also expressed in connection with the aerial spraying of oil-seed rape and potatoes, in particular.

(b) Yorkshire W.A.

In Yorkshire, the major concern lies with pesticide residues in non-water supply rivers (Edwards, pers comm 1985). In particular, the discharge of textile industry effluents into sewage works. Such industry commonly uses dieldrin, lindane and some pyrethroids for moth proofing. Of most concern are the levels of lindane (HCH containing 99 percent gamma isomer, an OC insecticide) which often exceed the EEC limit in affected rivers by two or three times. Lindane is used mostly by the wool textile industry to treat incoming fleeces.

Apart from the problems experienced in the industrialised south of the Y.W.A. area, some pesticide pollution of a localised nature is also in evidnce in the rural north, which provides most of the water supply. However, most of these problems involve spillages, for example, of diquat into the River Calder.

(c) Anglian W.A.

To date, Anglian W.A, has produced the most informative assessment of herbicide pollution at least (Croll, 1984). In 1982, the authority initiated a survey of all its water resources and included in it, analysis for a number of common herbicides, notably MCPA, Mecoprop, MCPB, 2,4-D, atrazine and simazine. Up to September 1984 concentrations of Mecroprop were found ranging from 0.2 to 2.7 μg/l in surface waters and 0.2 to 0.4 μg/l in groundwaters. MCPA was detected less frequently than mecoprop in surface waters (0.2 to 2.3 μg/l) only. Also, 2,4-D was detected less frequently than either of the above in surface waters at levels of 0.2 to 2.5 μg/l and in underground waters at 0.2 to 2.5 μg/l. Meanwhile, atrazine was found in almost all surface waters at concentrations of 0.2 to 1.4 μg/l, but less frequently in groundwaters (0.2 to 0.5 μg/l). Croll (1984) concluded that it was more likely that its presence at most points arose from total weed control on railway embankments, roadsides and industrial areas, rather than an agricultural use. Lastly, while simazine was detected at most sites where atrazine was found. Levels were generally only 25% of those of atrazine. Although the concentrations detected are

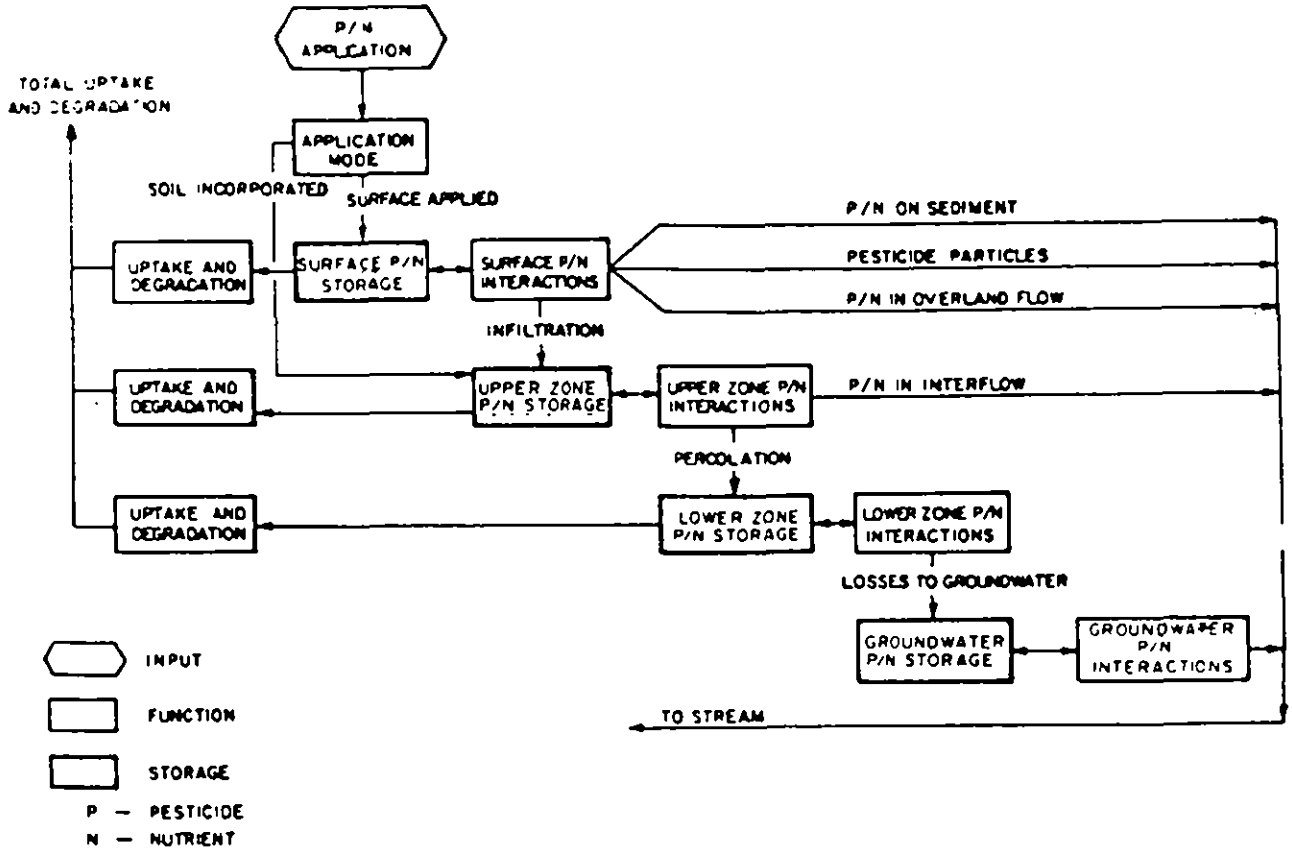


FIGURE 5 Pesticide and nutrient movement in the ARM model

Source: Skogerboe (1982)

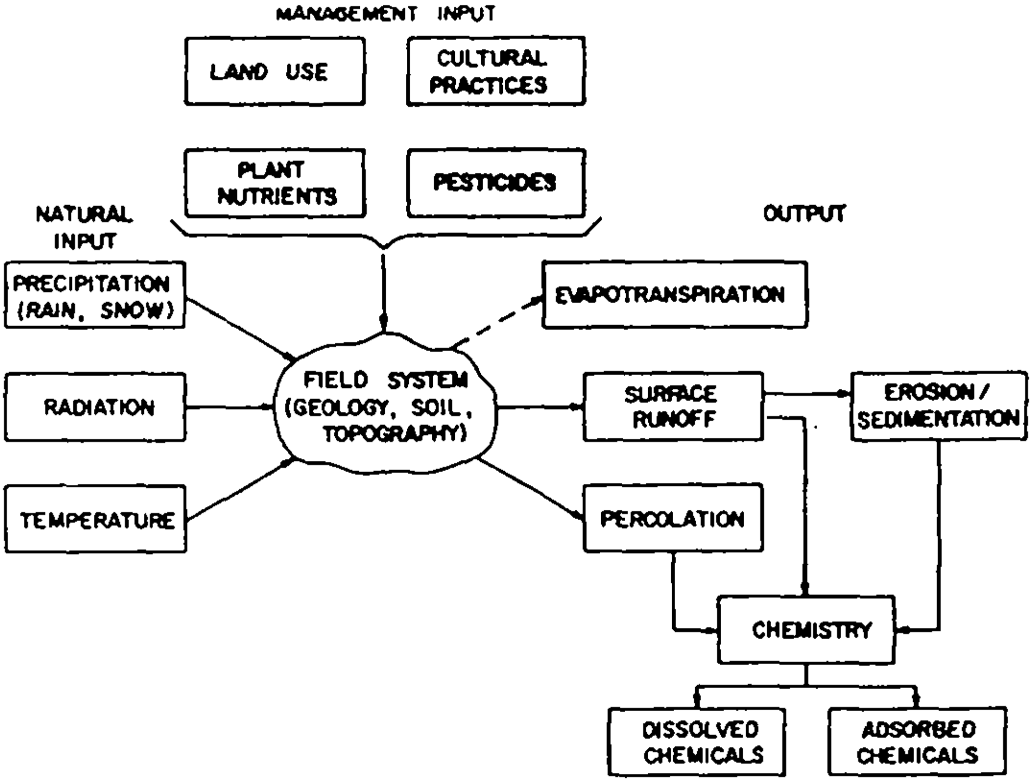


FIGURE 6 System for evaluation nonpoint-source pollution.

Source: Kuisel (1982)

The hydrology component estimates the water balance elements with options for calculating direct runoff. One option requires daily rainfall, the other, hourly or intensity data and uses an infiltration equation to partition rainfall into infiltration and direct runoff. The hydrology component calculates storm runoff volume and peak rate, storm rainfall energy, percolation, and soil water accretions for each storm event. Between storm events, evaporation, transpiration, percolation, and soil water content are calculated.

The erosion component calculates rill and interrill erosion, transport and deposition for any shape of overland flow profile. Sediment transport from overland flow is inputted to the concentrated-flow area or channel. Sediment yield at the field edge and sediment enrichment ratios, based on particle-size distribution, are calculated for use in the chemistry component.

The chemistry component considers both plant nutrients and pesticides. It calculates water and sediment fractions of pesticide load for the field. Foliar applied, soil-surface applied, and soil incorporated pesticides are considered. Multiple applications can also be simulated.

Nutter et al (1984) have simulated herbicide concentrations in stormflow from small forested watersheds using the CREAMS breakpoint hydrology and pesticide options. CREAMS accurately predicted hexazinone concentrations (a triazine herbicide) in the initial stormflow, but underestimated concentrations in stormflow two months or more after the application. In addition, the daily rainfall option of CREAMS was used to evaluate the relative risk of bromacil, picloram, dicamba, and triclopyr, as well as hexazinone, appearing in stormflow, following their application. The model predicted the following order of potential residue appearance in stormflow: bromacil   triclopyr   hexazinone   picloram   dicamba. In general, hexazinone losses averaged 0.53 percent of that applied. The underestimates for hexazinone after the first 75 days may have been due to a change in the source of the pesticide during stormflow (Nutter et al, 1984). Clearly the current version of CREAMS which does not account for subsurface movement, tends to underpredict concentrations which may be influenced by subsurface interflow.

c) A Simple Pesticide Runoff Model (Haith, 1980)

Although runoff is not the only pesticide transport mechanism, it may in many situations be the most significant pathway for entry to aquatic systems. Data from field studies provide a valuable means of estimating losses in runoff. However, these losses are influenced by many factors in endless combinations. Hence, the principal methods available for site and pesticide specific analyses of pesticide runoff are likely to be mathematical models.

There appears to be a need for a relatively simple pesticide runoff model which can be used to evaluate lossses for a wide range of field conditions and pesticide characteristics (Haith, 1980). The model proposed is based on commonly used methods of runoff and soil loss prediction, employing mass balance considerations of the surface 1 cm of soil. Below this depth, the pesticide is considered unavailable for runoff loss. Pesticide levels in the soil are also considered to decay exponentially with time. Meanwhile, total pesticide can be divided into adsorbed (solid-phase) and dissolved forms. The model can also allow for rainstorms subsequent to the first storm. To complete the pesticide runoff model, runoff and soil is also predicted, and is based partly on a modified Universal Soil Loss Equation (USLE) used to estimate soil loss from any rainfall event.

The model was tested (Haith, 1980) using data for atrazine losses for two small watersheds in Watkinsville, Georgia, applied as a surface spray to loosely tilled soil. Predicted and measured runoff, sediment, and atrazine losses for runoff-producing storms were presented. The accuracy of predictions varied among events showing that the model is not a suitable means of predicting losses from a single isolated storm. However, an estimation of average or seasonal losses are predicted fairly well. The total dissolved losses are more accurately predicted than solid-phase (adsorbed) losses.

d) An evaluation of some available pesticide runoff loading models.

Lorber and Mulkey (1982) tested three runoff models: ARM, Continuous Pesticide Simulation (CPS) and CREAMS, comparing them for their abilities to predict the movement of toxaphene and atrazine, using watershed studies in the Mississippi delta region. All the models accurately reproduced field data. For the CPS and ARM models, predictions of total erosion differed from observations by 6%, whereas CREAMS underpredicted erosion by 25%. Model predictions of total runoff differed from field observations by 15% or less. All models were within 10% of observations of overland toxaphene loss predictions but their predictions of peak events did differ. ARM could predict higher losses of soluble chemicals than the other two, due to its unique interflow component. Similarly, CREAMS estimation of sediment enrichment resulted in higher toxaphene loss predictions than the other two.

1.9 Conclusion

Pesticide usage continues to increase in the U.K. so that concern with the possible effects on river catchments, especially on water quality will also continue. While the move away from the more persistent organochlorine pesticides is to be welcomed, the increasingly large quantities of OP's, pyrethroids and carbamates being applied need careful investigation with regard to their possible residue levels to be found in British rivers. Herbicides probably represent the area of most concern since their total applications dominate pesticide usage in the U.K., aerially and quantitatively.

Many factors influence the behaviour and fate of pesticides after contact with soil, including such factors as adsorption, leaching, volatilisation, erosion, microbial degradation, chemical degradation and hydrolysis. All of the above are in part dependent on soil characteristics as well as the chemical characteristics of the pesticide. Moreover, soil erosion in agricultural areas is a major process contributing pesticides to the aquatic environment. Other sources, however, include industrial and sewage effluent and accidental spillages. All of these factors and sources need to be taken into consideration in any general study of pesticides in catchments, and in any modelling exercise.

More specifically with regard to pesticides in rivers, the present E.E.C. drinking water standards appear hopelessly misguided and open to disregard since a global standard of 0.5 ug/l for the total pesticides present takes no account of the toxic nature of individual compounds. Certainly, this is the view of Thames W.A.

Recent studies both in Australia and North America, meanwhile, seem to indicate that the actual losses of pesticide rarely exceed 5% of the total, applied, and as such are not alarming. However, what is of concern is the nature of the individual pesticide concentrations reaching rivers and their possible toxic effects on aquatic fauna. Clearly, storms following recent applications of pesticides represent the main period of concern since the changeover to less persistent pesticides.

The present water authority perspective on the possible pollution problems represented by pesticides varies. Thames W.A. experience "apparent" problems with the herbicides atrazine and simazine in relation to the levels present in supply waters. Yorkshire W.A., however, experience more urgent problems based on the industrial discharges of lindane in particular, from textiles maanufacturers, while Anglian W.A. have some evidence of elevated atrazine levels, probably due to indiscriminate urban usage.

Finally, with regard to the possibility of modelling pesticide movement within catchments, work in the U.S. suggests its feasibility. Certainly, the ARM and CREAM models offer good examples, although they both have obvious limitations. All such models require hydrology, erosion and chemical components, if they are to successfully model pesticide losses. Data inputs to them also require in many instances, detailed field observations and careful calibration and validation. Such procedures would thus also be necessary for any model derived by the authors for the British context. It is hoped that the feasibility of designing such a model can be fully assessed by the end of the present contract.

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