APPLICATION OF QUASAR TO THE YORKSHIRE OUSE

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1 Introduction

1.1 WATER QUALITY MODELLING

River water quality models need to represent the physical, chemical and biological transformations which occur within a river, so that, for a given set of inputs, water quality (WQ) both within the river reaches and at the outflow can be determined. The number and detail of processes represented, varies according to the purpose of the model and the required determinands. Crabtree (1986) highlighted the tendency of developing WQ models for specific types of problems and defined six types of river-quality problems which relate in part to the pollution source. These problems are, setting effluent standards, agricultural and diffuse rural runoff, non-point urban discharges, real-time operational control, the fate of toxic substances and finally pollution incidents. Although the processes which need to be modelled for each of these purposes may be similar, the significance of the processes may vary. Hence, depending upon the purpose of the river WQ model, its characteristics can be quite distinct. Table 1 identifies several models of interest and compares the determinands modelled and how each determinand is treated. These models are also briefly described in this Section.

Within the UK, the National Rivers Authority (NRA) uses some form of conventional deterministic model within a probabilistic framework to set consent standards: flow and quality data are derived from statistical relationships and are repeatedly passed through a model to build up probability distributions for the simulated quality determinands. There is currently a choice of three models: TOMCAT (Bowden and Brown, 1984), SIMCAT (Warn, 1987) and QUASAR (Whitehead et al, 1991). TOMCAT is based on a simple mass balance and simulates the distribution of flow, plus the concentrations of key determinands describing the interactions between biochemical oxygen demand (BOD) and dissolved oxygen (DO) within a river. SIMCAT is a similar catchment simulation model also based on a simple mass balance equation for effluent pollution, but here the variability of the polluting load and the variability of the dilution provided by the river is combined to produce a variable river quality downstream of the discharge. QUASAR similarly describes river BOD-DO interactions with the additional facilities of including algal influences on BOD, and it may be used in a dynamic mode to forecast WQ at any point in a dendritic river network. The hydraulics in QUASAR, TOMCAT and SIMCAT are also based on solutions of various approximations to the kinematic wave equation.

Table 1: Comparison of several river WQ models.

MODELLED DETS.	*QUASAR (Whitehead 1991)*	*TOMCAT (Bowden 1986)*	*SIMCAT (Warn 1986)*	*Yorkshire model (Holmes 1982)*	*R. Blackwater model (Caspieri et al. 1978)*	*QUAL-II (US. EPA. 1981a,b)*
Flow	Mass balance with time cons. (CSTR)	Mass balance with time cons. (CSTR)	Mass balance with time cons. (CSTR)	Steady state, Mass balance (CSTR)	Steady state, Mass balance (CSTR)	Steady state, Mass Balance (CSTR)
Conserv.	Yes eg. Cl	Yes	Yes eg. Cl	Yes	No	Yes
Temp.	Yes, conserv.	Yes, thermal transfer to reach air temp.	No	Yes, thermal transfer to reach air temp.	No set to temp of inflow for each reach	Yes
pH	Yes, conserv	No	No	No	No	No
Alkalinity	No	No	No	No	No	No
N	Yes NO_3, NH_4	Yes NO_3 NH_4	Yes NO_3 NH_4	Yes NO_3 NH_4	Yes NO_2 NO_3 NH_4	Yes NO_2 NO_3 NH_4
P	No	No	No	No	No	PO_4
C	No	No	No	No	No	No
DO	Yes	Yes	Yes	Yes	Yes	Yes
BOD	Yes	Yes	Yes	Yes	Yes	Yes
Algae	Yes, Cl_a included but not modelled	No	No	No	No, plant resp. and photosyn. is modelled	Yes, Cl_a modelled
Bacteria	No	No	No	No	Yes, Nitrosomonas	No
E-Coli	Yes	No	No	No	No	Yes
Bed-water column interaction	Yes sink terms	No	No	No	Yes bed respiration	Yes sink terms
Suspended sediment	No	No	No	Yes settlement and re-suspension	No	No
Turbidity	No	No	No	No	No	No
Salinity	No	No	No	No	No	No
Si	No	No	No	No	No	No
Metals	No	No	No	No	No	No
Pesticides	No	No	No	No	No	No
Organics	No	No	No	No	No	No
Other chemicals	No	No	No	No	No	No

Table 1 (cont): Comparison of several river WQ models.

MODELLED INPUTS	*QUAL2E (US. EPA. Brown 1987)*	*WASP5 (Ambrose 1991)*	*EXAMS (Burns 1982)*	*ECoS (Harris 1993)*
Flow	Mass balance with time cons. (CSTR)	1d advection-dispersion eqn.	Steady state or dynamic mode (CSTR)	1d advection-dispersion eqn. Tidal or tidally averaged.
Conserv.	Yes	Yes	Yes	Yes
Temp.	Yes	Yes	Yes	No, sinusoidal cycle
pH	No	Yes	Yes	Yes
Alkalinity	No	No	No	Yes
N	Yes NO_2 NO_3 NH_4 Organic N	Yes NO_3 NH_4 Organic N	Yes depends on organic species	Yes
P	Yes Organic P Diss. P	Yes Organic P Diss. P.	Yes "	Yes
C	No	CO_2	Yes "	Yes Organic C, CO_2 CO_3
DO	Yes	Yes	Yes	Yes
BOD	Yes	Yes	No	Yes
Algae	Yes, Cl_a	Yes, Cl_a	No	Yes, Cl_a
Bacteria	No	No	No	No
E-Coli	Yes	No	No	No
Bed-water column interaction	Yes sink terms	Yes, bed and subsurface bed deposition	Yes, sediment sorption	Yes, sink terms and 1d ad-disp. eqn. for bed.
Suspended sediment	No	Yes, particulate and dissolved	Yes, sediment sorption	Yes, 1d ad.-disp. eqn.
Turbidity	No	No	No	Yes
Salinity	No	Yes	No	Yes
Si	No	Yes, no algae interaction	Yes depends on organic species	No
Metals	No	Yes	Yes "	Yes eg. Cd, Zn
Pesticides	No	Yes	Yes "	Yes
Organics	No	Yes	Yes "	Yes
Other chemicals	No	No	Yes "	Yes eg TBT

Mathematical modelling of the WQ of the industrial rivers of Yorkshire was initially attempted by Holmes (1982) using what is known as the Yorkshire model. This is a steady-state model predicting BOD, DO, ammonium, suspended sediment and chloride in a deterministic manner using first order rate equations for the biochemical reactions. A simple mass balance equation is used for the flow routing part of the model. The River Aire upstream of the River Calder was studied, with the model calibrated to represent average conditions in summer 1978. Scenarios for future sewage works effluent loads were developed and an estimate of the state of the river in terms of flow and BOD made, assuming no improvement in sewage works technology.

Deterministic consent-setting models have also been developed within the USA, for example QUAL-II (Roesner et al., 1981). This type of model is designed to establish discharge standards set for specific polluting activities without reference to the receiving water. Instead, critical periods of high temperatures and low flows are studied under steady state flows. The resulting model is biochemically complex and based mainly on modelling the interactions between BOD and DO. The major constituent interactions of QUAL-II involve ammonia, nitrite, nitrate, benthic demand, carbonaceous BOD, phosphorus, chlorophyll-a and oxygen. In Crabtree (1986), this model was compared with another steady-state model, originally developed by the UK Water Research Centre: the site specific River Blackwater model (Knowles and Wakeford, 1978). In this model, phosphorous and chlorophyll-a are not described, but the growth of Nitrosomas bacteria is explicitly included and controls the nitrification rates. After calibrating the model transformation rate coefficients it was concluded that the QUAL-II model produced a closer prediction than the Blackwater model, when compared with observed data from the River Blackwater.

The QUAL2E version of QUAL-II has the additional facility of dynamically simulating transport in a branching river system. In this model the 1D advection-dispersion mass transport and reaction equations which describe the sysytem are solved by an implicit finite difference scheme. Uncertainty analysis techniques are also incorporated which allow the user to obtain a sensitivity analysis of the parameters and an error analysis of the predictions and observations.

The Water Quality Analysis Simulation Program (WASP5; Ambrose et al, 1991) is a US Environmental Protection Agency (EPA) model developed as a general tool for predicting WQ responses to natural phenomena and man-made pollution. The time-dependent processes of advection, dispersion, point and diffuse mass loading, and boundary exchange are represented in the model. It is therefore an example of a dynamic model for aquatic systems, including both the water column and the underlying benthos system. The major determinands modelled are BOD, DO, nitrogen, phosphorus and phytoplankton variables. Various levels of complexity can be used to simulate these variables and interactions. To simulate only BOD and DO, for example, the user may bypass calculations for the other variables, or, at the other extreme, include a simulation of intermediate eutrophication kinetics with benthos reactions. Another possibility is to simulate the transport and transformations of organic chemicals and up to three solid materials, with the chemicals linked through the reaction yields.

EXAMS (Burns, 1982) was developed in the US by the EPA to model the aquatic fate and transport of organic chemicals. The model simulates steady-state or dynamic transport of chemicals through a 1D advection equation with linked transformation rates. Within each segment or compartment, the processes modelled include ionisation of organic acids and bases and partitioning of the compound with sediments and biota. Transformations may be the result of photolysis, hydrolysis, biolysis and oxidation reactions. Up to 28 molecular species of one chemical may be modelled at one time in order to account for differences in reactivity occurring as a result of the differing chemical molecular forms.

ECoS version 2 (Harris, 1992) is an estuarine modelling shell developed by Plymouth Marine Laboratory to simulate estuarine dispersion and the fate of contaminants. Simulations in ECoS are reduced to 1D by considering only transport along the axis of the estuary, and sectionally-averaging the physical parameters. These simulations can be either tidally-averaged or they can be explicitly tidal. Three linked transport equations are solved: one for the water column, one for suspended particulates and one for mobile bed sediment. Dissolved contaminants can partition onto suspended material, and transfer to and from the bed of the estuary as exchanges with the mobile sediment. In addition contaminants can be lost to the atmosphere, and lost by degradation from the water, suspended particulates and bed sediment. The underlying transformation processes can be specified by the user so a determinand can be described to any level of complexity. Non-tidal simulations can also be carried out using inputs of freshwater runoff and associated chemicals.

There are thus a multitude of WQ models which may be chosen for a particular application, and this choice is related to the detail in which the river system is to be studied. Hines et al, (1975) outlined the increasing complexity possible in the various biochemical interactions that can be modelled. The increase in complexity is not a straight forward progression but approximately increases in the order of modelling conservative ions, through DO, temperature, ammonia and nitrate models, to indicator bacteria and sediment transport models, through algal growth, metal transport and nutrient and pesticide transport models and eventually leading to the most complex eutrophication processes.

The data requirements correspondingly increase as the complexity of the model's representation of the river system increases. A two-dimensional advection-dispersion model, for example, would require much more boundary data for the flow and chemistry than a simple steady-state model. However, the steady-state model will be inadequate in simulating the effects of intermittent storm events or pollution incidents on a river. A clear idea of the potential data requirements of the model with due consideration of the model's capabilities is therefore important in any modelling exercise.

The accuracy of a model's results can be affected by several of the following factors. Simplifications that the model makes about the river system can cause errors since a complete representation of the processes occurring within the system is not made. Numerical solution techniques used by the model also introduce some error but this can be controlled by the sensible choice of temporal and spatial increments. Inaccuracies in the input data, such as from inherently incorrect data sets or from inappropriate values used in the parameter set will also introduce errors. The influence of different types of error has to be checked and this may be done by carrying out a detailed sensitivity analysis of the model. It is inevitable then that a WQ model will have inaccuracies and so it has to be decided what level of error is acceptable. This associated error has to be considered when the model simulation results are analysed or compared to observations.

In any application of a WQ model, the procedures of calibration and validation have to be carried out. Both of these procedures are highly dependent upon good quality data. It has been said (Crockett, 1994) that when critical data is lacking, WQ modelling becomes more of an art than a science. The need to use a WQ model with incomplete and inadequate data sets often imposes more simplifications of the model's representation of a river system than that imposed by the model formulations themselves. For example, the description of a river system by a simple DO-BOD model can be seriously inaccurate if the correct inputs from sewage treatment works are not used. In the calibration exercise, various key parameters are first estimated and thereafter adjusted to achieve a good fit of the simulated model values to observations. The validity of any of these adjustments to the constants and coefficients need to be checked with published values. Once a model is calibrated it should be verified using a separate data set in which the errors produced between the simulated and observed values are generally larger than those in calibration. Large errors in the validation exercise may result in further changes to the model structure. Finally, once a model has been calibrated and verified, it may be used to simulate and investigate further changes to the river system.

1.2 QUASAR - QUALITY SIMULATION ALONG RIVERS

The QUASAR model (Whitehead, 1991) is an integrated WQ and non-tidal flow model, which combines the upstream river flow, inputs from tributaries, effluent discharges and losses due to abstractions, to calculate the flow and WQ in the river at points further downstream. Modelled constituents include flow, temperature, pH, a conservative quantity such as chloride, BOD, DO, nitrate and ammonium, forming a basic dynamic model for DO-BOD interactions. The model essentially performs a mass balance of flow and WQ determinands and allows for chemical and biological transformation processes down a river system. These decay processes at present are described by temperature dependent first order transformation rates. A complete description of the models components is given by Williams (1994). The differential equations used are also included in Appendix 1 of this report.

In this model a river is essentially idealised as a set of continuously stirred reactors. Each reactor has a residence time which is derived from knowledge of or calibration of the velocity-discharge relationship for the river reach and is therefore related to the discharge. This idealization of flow routing has been shown in Whitehead et al. (1979) to approximate the partial differential equation representations of advection-dispersion mass transport known as the kinematic wave equation. QUASAR's mathematical formulation for WQ is based on a set of ordinary differential equations which determine the changes in determinands over time for each reactor. These equations require lumped rate parameters which are determined by calibration, and which represent a simplification of the chemical and biological transformations occuring in the river system. The transformation rates also have an explicit temperature dependence.

The river system is thus divided up into reaches, with the reach boundaries determined by points in the river where there is a change in the WQ or flow. This may be due to the confluence with a tributary, the location of a sewage treatment effluent discharge, an abstraction, or the presence of a weir. Certain river stretches may have particular biological or chemical reactions and are dealt with by ensuring that appropriate reach boundaries are defined. The inputs to the model are generally termed point source since they can only be applied at certain discrete points along the river into each continously stirred tank and so into a particular reach. This terminology however can be misleading since diffuse inflows, if identified, can also be incorporated as an input albeit at a discrete location into each stirred tank.

2 The Yorkshire Ouse

2.1 PHYSICAL CHARACTERISTICS OF THE YORKSHIRE OUSE REGION

2.1.1 Geographical and Hydrological Background

The Yorkshire region of the NRA covers 13,500 km^2 and presents a wide range of landscapes exhibiting considerable diversity in their climate, topography, geology and land-use. Figure 1 shows the topography of the area. In terms of the hydrology of the region, six distinct topographical areas can be recognised. In this application of QUASAR to the Ouse system only two of these areas, the Pennines and the Vale of York, need be considered. A fuller description of the whole NRA region is given in the review of the 1988-1990 drought by Marsh et al (1991).

At the western boundary of the NRA region lies the north-south spine of the Pennines, in which the headwaters of the rivers Swale, Ure and Nidd rise to over 600 m OD. These rivers flow mainly in a south-easterly direction and form the characteristic ridge and valley topography of North Yorkshire. The Swale/Ure/Ouse system is composed of typically responsive rivers with large seasonal flow variations, whereas the River Nidd is highly reservoired in the headwaters, and so less responsive. Geologically the Yorkshire Pennines north of Skipton are composed of Carboniferous Limestone and strata of the Millstone Grit series.

To the east of the Pennines and running approximately parallel with them is the Vale of York. This is a low-lying area of subdued relief, through which the main rivers converge to form the River Ouse. The western edge of the Vale is composed of an escarpment of Magnesian Limestone, about 5 km wide. Directly to the east Triassic sandstone underlies the majority of the area, while in the eastern margins of the Vale the land is underlain by Keuper Marl. The principal aquifers in the region are shown by the outcrop areas in Figure 2. In terms of water volume abstracted, the Triassic Sandstone is the most important aquifer in the Ouse catchment.

The annual average rainfall (calculated for the period 1941-70) for the Yorkshire Region is shown in Figure 3. There is significant spatial variation in annual rainfall amounts due to the effects of elevation, rain-shadow and aspect. An appreciable west-east rainfall gradient is evident across the Yorkshire region. The wettest areas are located in the north west, where annual totals reach 1800 mm. In contrast, the Vale of York receives on average less than 700 mm of rain annually.

2.1.2 Land Use

The Pennine uplands consist largely of an expanse of moorland used predominantly for rough grazing, with the valley floors under permanent pasture. The Vale of York is intensively cultivated arable land. Woodland is sparse.

In the Ouse catchment, population is centred at Richmond and Catterick on the upper Swale and at Northallerton and Thirsk on tributaries of the lower Swale. On the River Nidd there are two main centres, at Harrogate and Knaresborough. The River Ure has one population centre at Ripon and the River Ouse has a large centre at York. There are also numerous villages and hamlets scattered along the main rivers and roads.

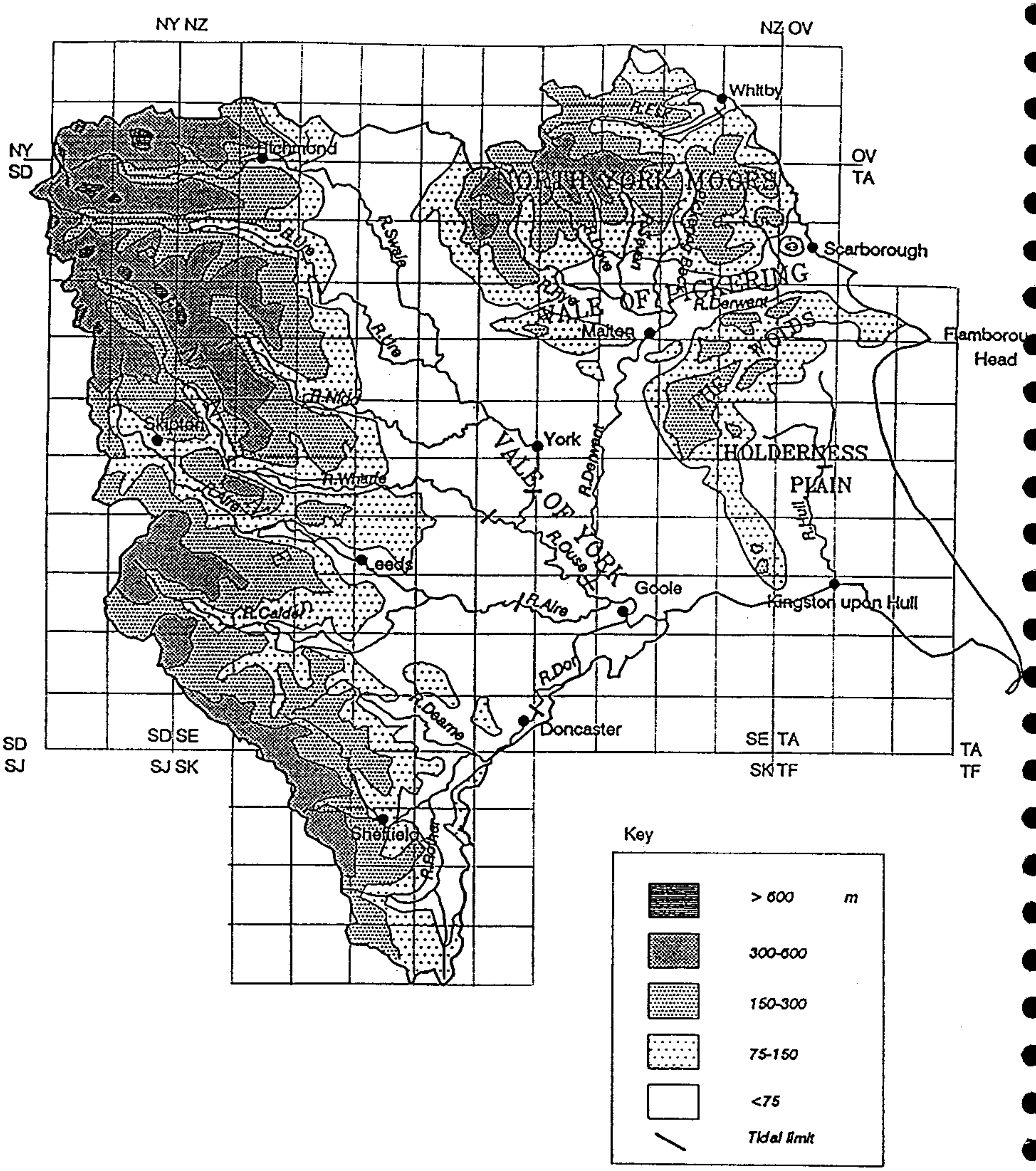


Figure 1 The Yorkshire NRA region

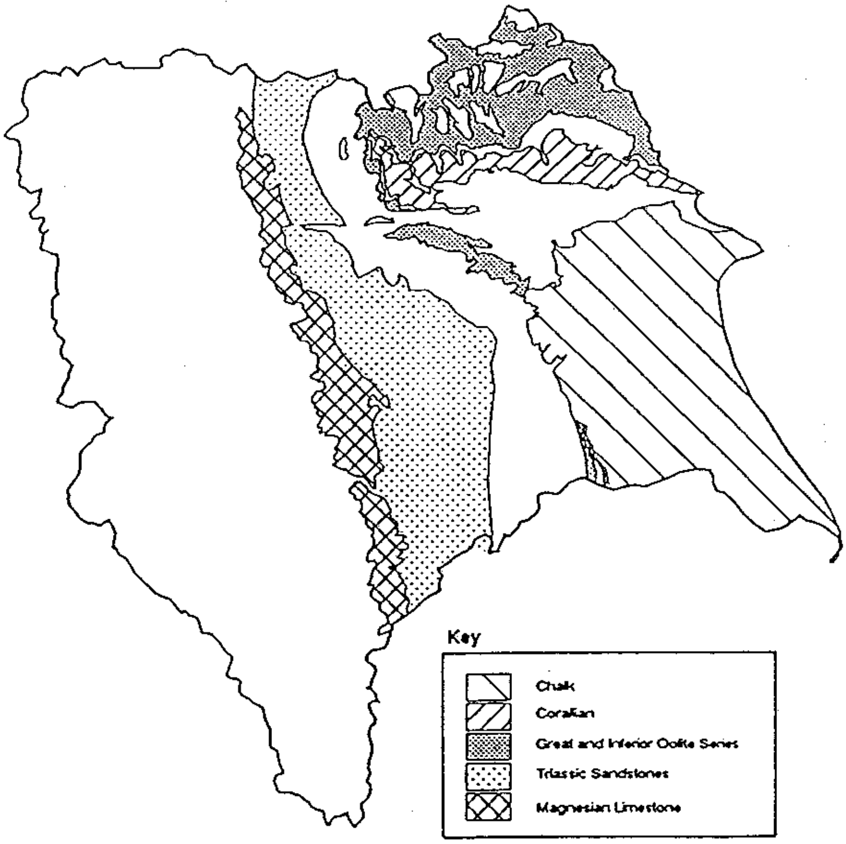


Figure 2 Outcrop areas of the Yorkshire NRA region

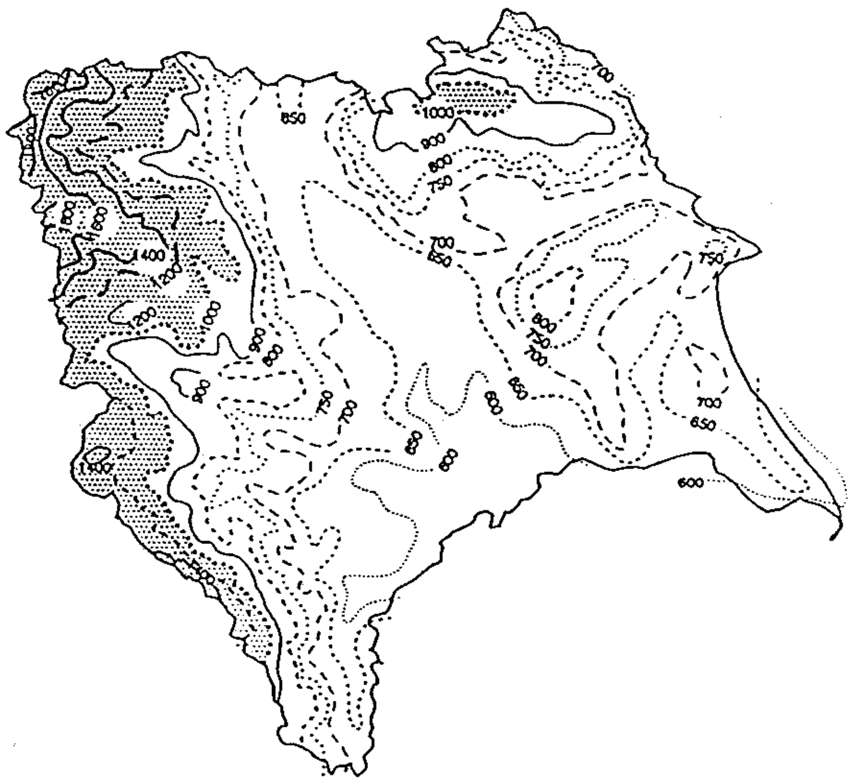


Figure 3 Annual average rainfall (1941-70) in mm

2.2 APPLICATION OF QUASAR TO THE YORKSHIRE OUSE

This report deals with the application of QUASAR to the Yorkshire Ouse above Skelton, near York. The model is applied to the major tributaries above Skelton, to simulate the transport of several conservative quantities (flow, temperature, pH and chloride) and a basic set of constituents determining the DO-BOD relationships in this system ie nitrate, ammonium, DO and BOD. In this initial investigation of the Ouse catchment, the modelling effort has been focused on the main river system, using observed input data where these are available. Where inflows of water and WQ are not available, an estimate of inputs has been made. Within the overall LOIS programme further refinements of these inputs using catchment delivery models is expected.

The River Ouse is described in terms of the three main rivers the River Swale, the River Ure which becomes the River Ouse at its confluence with the Swale, and the River Nidd. Figure 4 gives a representation of the river system in then Ouse catchment with the important inputs and WQ sites identified. QUASAR has been applied to the Ouse catchment above York using inputs representing the headwater catchments, major tributaries, significant abstractions and major polluting sources. Water quality data collected by the Northumbria/Yorkshire National Rivers Authority (NRA) are used, along with flow data from the National Water Archive (NWA).

Inevitably the application of the model to such a large catchment suffers from a large number of the tributary inputs not being monitored. The annual flow accumulations downstream were checked (Lewis, 1994a) to determine how far the NRA gauged data for the headwaters and monitored tributaries accounted for the observed flows at the downstream end of each main river system. Large discrepancies between the observed and cumulated flows were evident, with additional errors introduced by inaccuracies in the gauging stations. This analysis led to a further discretisation of the river network with additional tributaries being added. It was determined that for a good water balance, catchments with area > 20 km^2 along the rivers Swale and Ure and catchments with area > 5 km^2 along the river Nidd were required These tributaries are identified in Figure 5 and their annual mean daily flows (MF) as estimated using the IH Micro Low Flows (MLF) package. The calculation of these ungauged flows is detailed in Lewis (1994c) and outlined in Section 3.

Estimates of WQ are also required for these additional tributaries and procedures for this have been developed and are reported on in Section 3. Other inputs to the model include those from the major sewage treatment works (STW), water pollution control (WPC) works and trade effluents. These have been monitored by the NRA, with various determinands measured (usually including ammonium, nitrate, BOD and pH) on a monthly basis. Using a combination of the monitored inputs and estimated ungauged inputs QUASAR has been applied to the Ouse catchment with the river network defined in the next Section 2.3. The model was calibrated for the year 1990, using a daily input time series. The calibration procedure is described in Section 4 and the results of the calibration exercise is shown in Section 5. A sensitivity analysis of the model's biochemical rate coefficients and physical parameters is given in Section 6. Verification of the model is carried out with the three year data set 1/1/1991 to 31/10/1993, and a discussion of the results given in Section 7. Finally Section 8 discusses the conclusions of this work.

Figure 4 : Ouse catchment - main river network with NRA gauging stations, major water quality sites and main effluent and abstraction points

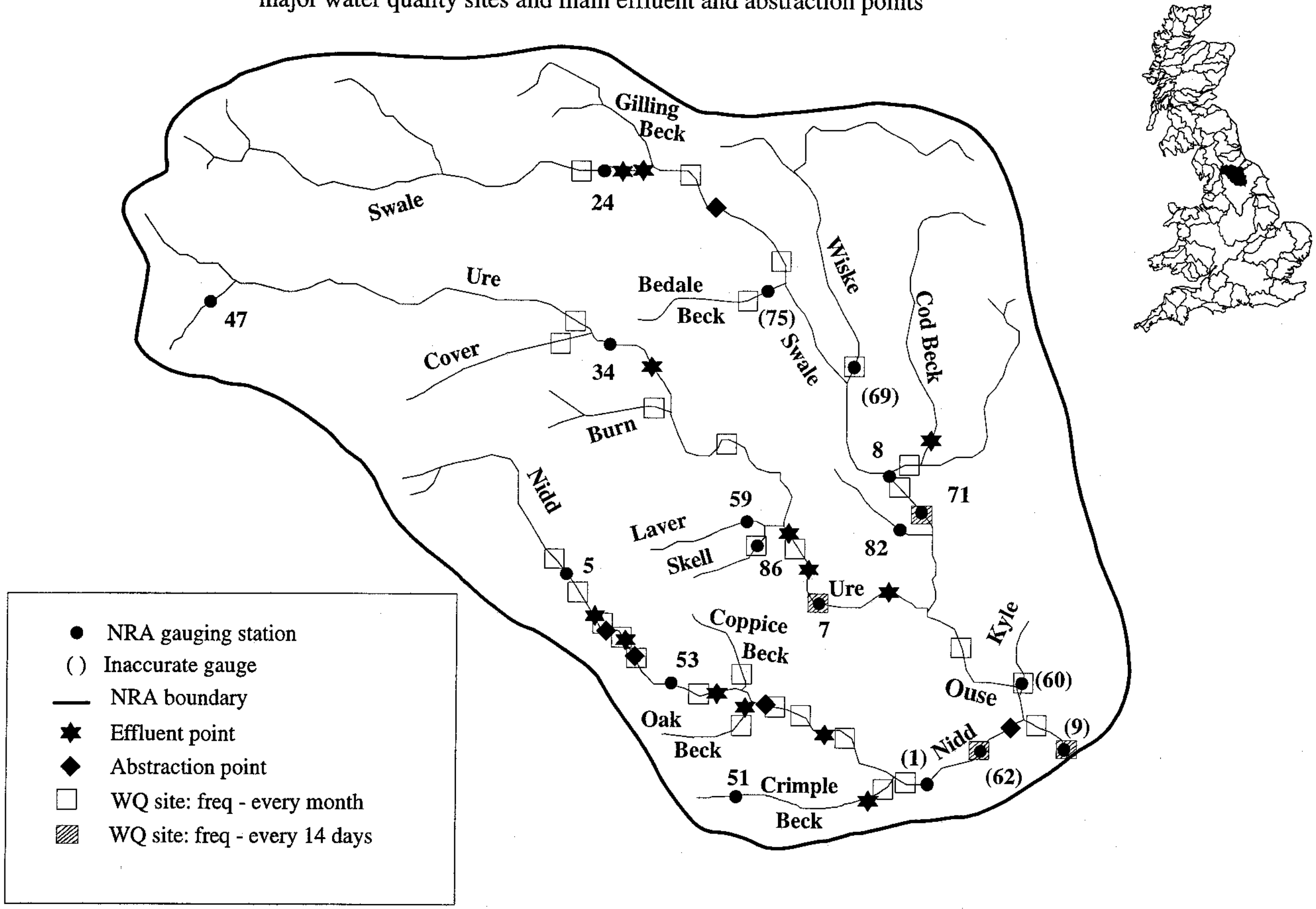
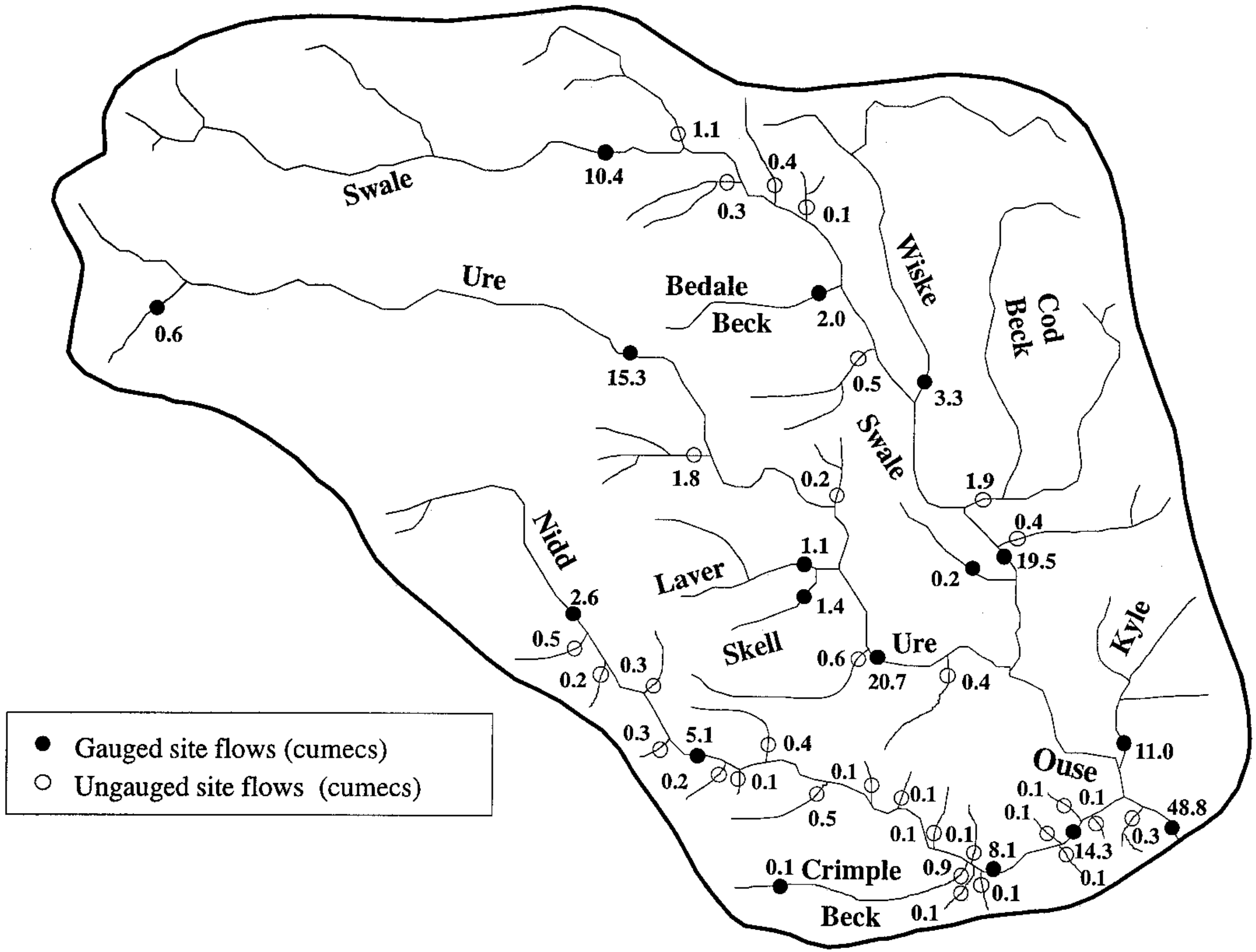


Figure 5 : Main tributaries and mean annual flows within the Ouse catchment.



2.3 THE QUASAR RIVER OUSE NETWORK

The QUASAR river network used is shown schematically in Figure's 4 and 5 in which the major rivers modelled are shown along with the major inputs and WQ sites. Table 2 gives a summary of the physical structure of the river network in which the total number of WQ sites includes those on monitored tributaries. Only the three main rivers - the River Swale, the River Ure, and the River Nidd - have been explicitly modelled. The River Ure becomes the River Ouse at its confluence with the Swale. The starting point for the simulation of each river is the headwater gauging station which has an associated WQ site, and the end points are either the confluence with the River Ure or, in the case of the River Ouse, the gauging station at Skelton, York.

In this modelling exercise each river is divided into reaches with the reach boundaries determined by points in the river where there is a change in the WQ or flow. These reaches are further sub-divided with a maximum length of 2 km for these sub-reaches. The reach boundaries are taken to be places in the river system where changes in the WQ occur, such as tributary confluences, effluent discharges, abstraction points or weir locations. Tributaries, effluent discharges and abstractions are treated as point source inputs into (or out of in the case of abstractions) the top of a particular reach. Weirs are located at the bottom of a reach since the reaeration processes occurring here affect the input to the next reach. As an example, the River Swale has a total of 16 reaches into which flow 10 tributaries and 2 effluent points with 1 abstraction out of the river. Reaches may also be included in the network to allow predictions to coincide with a measured WQ site. The River Swale then has a reach boundary at the confluence with the River Ure, which also has a reach boundary at this point in its river network.

The spatial accuracy with which the river network has been constructed is estimated at ± 125 m for each reach boundary and ± 250 m for the positions of the tributary, effluent and abstraction points and the WQ sites.

Table 2 *River network, including number of reaches, effluent points, abstraction points, number of tributaries and total number of WQ sites for each main river.*

River	No. of reaches	No of Tributaries	Effluent points	Abstraction points	No of weirs	Total no of WQ sites†	Total length (km)
Swale	16	10	2	1	1	8(3)	68.9
Nidd	26	18	6	4	13	14(3)	63.5
Ure	14	5	4	0	5	6(2)	44.5
Ouse	5	2	0	0	0	5(1)	14.6

† the figures in brackets show the number of WQ sites monitoring tributaries on that main river

3 Model Inputs

3.1 FLOW

Lewis (1994c) describes the calculation of the ungauged daily flows within the Ouse catchment. A transformation method (TM) was used for transferring daily gauged flow data to ungauged sub-catchments. This procedure requires gauged and ungauged sites to be grouped together according to some classification scheme. Estimates of the 95 percentile exceedance flow expressed as a percentage of the mean flow, as calculated by the MLF system (Gustard et. al., 1992), is used for the purpose of this classification. Based on similar catchments nearby, estimates of daily flows for all significant ungauged tributaries can then be made.

Section 3.1.1 gives a more detailed overview of the classification scheme used, and Section 4.2.1 considers the results of the water balance carried out in Lewis (1994c). QUASAR was used to calculate the flows in the major rivers with the gauged tributary flows and the important ungauged tributary flows included as point inputs in the simulation. Comparisons with the appropriate NRA gauging station flows were made at the bottom of each of the major rivers and at the furthest downstream point in the system.

3.1.1 Transformation method and classification scheme

It is assumed that similar catchments in the same area will produce a similar time series of daily flows. Consequently, if the daily flows and the relevant catchment characteristics are known for a gauged sub-catchment, then daily flows for an ungauged sub-catchment with similar catchment characteristics may be determined.

The time series transformation factor (TF) between sites is based simply on the catchment areas and average rainfalls, and is given by the equation

$$Q_u(t) = Q_g(t)\left(\frac{A_u}{A_g}\right)\left(\frac{SAAR_u}{SAAR_g}\right), \qquad (1)$$

where the subscripts g and u denote the gauged and ungauged sites, Q(t) is the daily flow time series (cumecs), A is the catchment area (km^2) and SAAR is the standard period (1941 to 1970) average annual catchment rainfall (mm).

The method of classifying sites is based on the MLF 95 percentile exceedance flow (Q95). In calculating the Q95 value for an ungauged site the MLF system uses a provisional classification scheme of 29 hydrological response (HOST) classes (Boorman et. al., 1990) with the addition of URBAN and LAKE classifications. These 31 classes are replaced by 12 Low Flow HOST groups. Using linear least squares multiple regression analysis, expressions relating the percentage of Low Flow HOST classes and Q95 values for 865 gauged catchments were obtained (Gustard et. al., 1992). The 95 percentile exceedance flow at ungauged sites is then estimated by the MLF system from the fraction of Low Flow HOST classes present within the catchment.

It is useful to express the MLF Q95 values as a percentage of the mean flow (Q95%), since this adjusts for the size of the catchment. Two catchments are assumed to have similar hydrological responses if their MLF Q95% values are of similar magnitude. A high Q95% value indicates that the catchment response is predominantly due to base flow, the catchment has permeable soil and is dominated by ground water. In contrast, a low Q95% value indicates that the catchment is flashy, has an impermeable soil and the response is mainly due to direct runoff.

In choosing the gauging stations from which transformations are calculated only gauging stations monitoring a tributary should be considered and not main river stations. The flow must not be heavily controlled by reservoirs and the catchment should preferably be near to the ungauged site. The calculation of the ungauged daily flows are of course approximate since annual totals are used to transfer the gauged daily flows. A further approximation is introduced through the use of the hydrological response classification scheme since sizable differences can exist in the Q95% values for the two catchments.

In order to choose gauging stations which are suitable for transferring data to ungauged catchments the above criteria were used and only six gauging stations were deemed suitable for estimating the daily flows. These were in turn, grouped together into three classes of Q95% values, termed low, medium and high. In matching ungauged sites to gauged sites, the Q95% class gives a first estimate. Within a class, the matching is then based on the closest values of Q95%, followed by the SAAR and the MF values and the proximity of the catchments.

Estimates for the MF of the significant ungauged tributaries on the rivers Swale, Ure, Nidd, and Ouse are given in Lewis (1994c), with the appropriate gauging stations to which the tributaries are matched and the required transformation factors.

3.2 WATER QUALITY

3.2.1 Water Quality Monitoring

This Section describes briefly the WQ monitoring carried out within the Ouse catchment by the Northumbria/Yorkshire NRA. Emphasis is given to the classification scheme used by the NRA with a view to estimating WQ for ungauged tributaries.

Northumbria/Yorkshire NRA is responsible for maintaining and improving WQ in the rivers in the Ouse catchment. Their stated objective (Yorkshire NRA report, 1986) is to gradually improve the quality of polluted rivers so that eventually all rivers and tributaries become at least Class 2 quality. Regular monitoring is carried out to determine both the overall state of the water environment and the factors which affect quality such as sewage and trade effluent.

The Ouse and its tributaries are predominantly of good to fair WQ above Skelton; all of the main rivers are of Class 1 quality as are most of the tributaries, only four tributaries are of Class 2 and one tributary of Class 3. Table 3 gives details of the NRA classifications of the main rivers at the monitored WQ sites downstream of the headwaters and the monitoring frequency of the river during 1990. In addition to these main river sites there are two or three tributaries monitored on each main river, and these generally tend to be polluting tributaries. Table 4 gives details of the WQ monitoring at these sites. Generally WQ is sampled on a monthly basis except for the furthest downstream main river WQ sites which are monitored every 2 weeks. The set of QUASAR determinands are measured for each site.

For tributaries of Class 2 (fairly good quality) and Class 3 (poor quality), the degradation in river water quality is generally due to the input from sewage discharges. Table 4 identifies the major effluent outlets into these tributaries. There are in some cases (e.g. Crimple Beck) several WQ sites monitoring a tributary. In general, the WQ sampling sites used in this work are those nearest the main river, and these sites are usually downstream of any sewage inflows. The pollutant load is then explicitly included in the modelling exercise. Oak Beck is the only exception to this, where the Harrogate (north) STW outflow is downstream of the WQ site and so has to be included in QUASAR as a separate point effluent source.

Table 3 *WQ sites on the main rivers in the Ouse catchment and the NRA classification at that point*

River/ Downstream order	WQ site name	NRA classification	Distance from head-water (km)†	No of observations (1990)
Swale				
1	Hudswell (Lownethwaite)	1a	-5.0	12
2	Catterick	1b	9.3	12
3	Morton-on-Swale	1b	28.1	12
4	Topcliffe	1b	53.6	12
5	Brafferton (Thornton Bridge)	1b	61.6	26
Nidd				
1	Pateley Bridge	1a	-5.0	12
2	Inlet to Glasshouses Trout Farm	1a	4.9	6
3	Below Glasshouses Trout Farm	1a	6.6	6
4	Inlet to Low Laithe Trout Farm	1a	7.7	6
5	Below Low Laithe Trout Farm	1a	8.8	12
6	Killinghall (A61 Road Bridge)	1a	19.6	12
7	Scotton Mill weir	1b	25.6	12
8	Knaresborough	1b	29.5	12
9	Below Knaresborough STW	1b	34.8	12
10	Walshford Bridge	1b	42.1	12
11	Skip Bridge	1b	57.5	26
Ure				
1	Wensley Bridge	1a	-10.0	11
2	West Tanfield	1b	17.5	11
3	Hewick Bridge	1a	29.5	11
4	Boroughbridge	1a	40.0	11
Ure-Ouse				
1	Aldwarke Bridge	1b	49.8	26
2	Moor Monkton (Nidds mouth)	1b	52.8	0
3	Moor Monkton (storage channel)	1b	54.0	0
4	Nether Poppleton (Skelton)	1b	59.1	26

† The first entry for the Swale, Nidd and Ure rivers is the headwater WQ site and if it is upstream of the NRA gauging station a negative distance is given

Table 4 *Water quality sites on the tributaries of the main rivers in the Ouse catchment*

River/ Downstream order	WQ site name	NRA classification	Major STW or WPC	Distance from headwater (km)	No of observations (1990)
Swale					
1	Bedale Beck at Leeming	2	Bedale WPC	30.3	12
2	River Wiske at Kirby Wiske	3	Northallerton STW	40.7	12
3	Cod Beck at Topcliffe	2	Thirsk STW	55.6	12
Nidd					
1	Coppice Beck	1b		20.8	12
2	Oak Beck at A61 bridge	2	Harrogate STW (N)†	23.5	12
3	Crimple Beck at Little Ribston	2	Harrogate STW (S)	41.1	12
Ure					
1	River Burn at Masham	1a		9.4	11
2	River Skell at Woodbridge	1b		29.5	11
Ure-Ouse					
1	River Kyle at Newton-on-Ouse	2	Tollerton and Tholthorpe STW	50.7	11

† the WQ site is upstream of the sewage discharge outlet

3.2.2 Water Quality Classifications

The National Water Council (NWC) classification scheme (Appendix 2) is based upon the monitoring of three chemical determinands: DO, BOD and ammonia. These determinands are indicators of the extent to which waters are affected by wastewater discharges from sewage or trade industries and run-off from rural land containing organic, degradable material (NRA 1994). Using the NWC classifications for all rivers a matching scheme for gauged and ungauged tributaries can be employed in modelling the basic DO-BOD interactions in a river system.

Gauged and ungauged tributaries are matched using the NWC river classifications (Appendix 2) for all rivers and the Institute of Terrestrial Ecology (ITE) 1 km^2 land cover data set (Fuller, 1994). The matching procedure for an ungauged tributary is to take the nearest WQ gauged tributary as the matching WQ station, provided that it has a similar NRA classification and the land use is similar for the two catchments. Figure 6 shows the ITE land use data set for class 18: tilled land, which is of most use in this classification scheme. This classification indicates agricultural usuage where inputs of N are expected to be relatively high. A black pixel indicates 100% and white 0% of tilled land. Ideally a detailed breakdown of the percentages of each ITE class in each catchment is required for a comprehensive comparison of two catchments. In this work only an eyeball fit is used to determine the similarity.

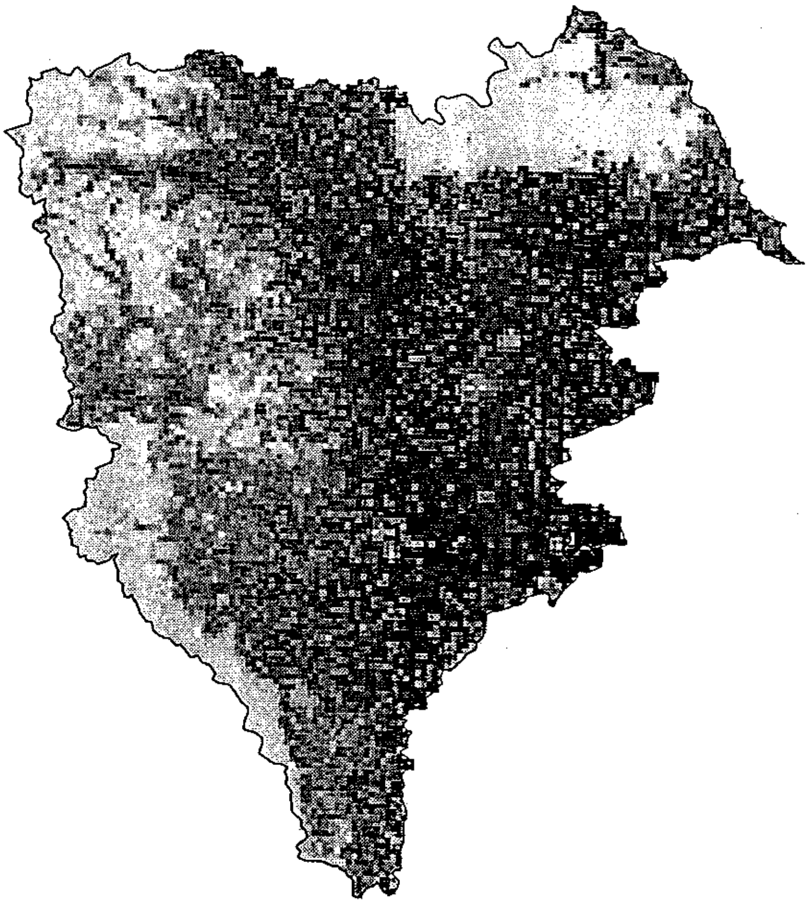


Figure 6 ITE class 18 : Tilled land

Monitored tributaries tend to have an associated STW which leads to some depreciation of the waterway, however this anthropogenic effect is represented in the tributaries NWC classification. In making the WQ classification for an ungauged tributary, the presence of an associated STW on the monitored tributary is implicitly included through the rating given by the NWC river classification. No attempt was made to naturalise the monitored catchment WQ values by extracting basic loads input into the tributary from the STW. Tables 5 to 8 identifies the ungauged tributaries on each river system and their matched WQ sites according to these classifications (the ungauged number in these tables refer to WQ monitoring and not to flow as some of the tributaries e.g. Cundall Beck is flow monitored).

The ungauged inputs are then taken to be the same as those for the matched gauged WQ site. Monitored values are linearly interpolated to produce a daily variation, and this time series is then used as the WQ input to QUASAR. This daily interpolation may be the cause of some problems, but it is an improvement over using monthly values for the inputs. A further refinement would be to introduce flow weighted interpolated values.

Table 5 *Tributaries on the River Swale (catchment area ≥20 km^2) with their NRA classification and matched WQ site.*

Ungauged number	Grid Ref.	Trib name	Area (km^2)	NRA classification	Matched WQS
Richmond	NZ146007	Swale at Richmond	384.50	1a	Richmond
1	NZ212000	Skeeby Beck	83.00	1a	Richmond
2	SE249973	Brough Beck	25.00	1a	Richmond
3	SE289966	-	45.50	1b	Richmond
4	SE302958	The Stell	21.25	1b	Richmond
		Bedale Beck	160.30	2	Bedale
5	SE340860	Old Stell	61.50	1b	Bedale
		River Wiske	215.50	3	Wiske
	SE413750	Cod Beck	218.75	2	Cod
6	SE432733	-	51.25	1b	Cod
7	SE431716	Cundall Beck	36.75	1b	Cod

Table 6 *Tributaries on the River Nidd (catchment area ≥5 km²) with their NRA classifications and matched WQ site.*

Ungauged number	Grid Ref.	Trib name	Area (km²)	NRA classification	Matched WQS
Gouthwaite	SE141683	Gouthwaite Res.	113.70	1a	Gouthwaite
1	SE151664	Ashfold Side Beck	20.00	1a	Gouthwaite
2	SE162648	Greenhow Sike	10.50	1a	Gouthwaite
3	SE189639	Near/Far Beck	16.25	1a	Gouthwaite
4	SE201601	Darley Beck	16.50	1a	Gouthwaite
5	SE253589	-	11.00	1a	Gouthwaite
6	SE269590	-	7.25	1b	Gouthwaite
	SE286597	Coppice Beck	24.00	1b	Coppice
	SE304583	Oak Beck	36.00	2	Oak
7	SE363571	-	5.00	1b	Coppice
8	SE372569	-	8.00	1b	Coppice
9	SE387544	-	11.75	1b	Coppice
	SE405531	Crimple Beck	83.75	2	Crimple
10	SE413534	-	14.00	1b	Coppice
11	SE418524	-	13.75	1b	Coppice
12	SE420522	-	13.00	1b	Coppice
13	SE466543	Sike Beck	9.75	1b	Coppice
14	SE473551	-	6.50	1b	Coppice
15	SE484564	Whixley Cut	13.75	1b	Coppice
16	SE499563	-	6.50	1b	Coppice

Table 7 *Tributaries on the River Ure (catchment area ≥20 km²) with their NRA classifications and matched WQ sites.*

Ungauged number	Grid Ref.	Trib name	Area (km²)	NRA classification	Matched WQS
Kilgram		Kilgram Bridge	510.20	1a	Kilgram
1	SE230798	River Burn	97.00	1a	Burn
2	SE322736	Nunwick Beck	30.00	1a	Kilgram
-		Rivers Skell and Laver	120.25	1b	Skell
3	SE347672	-	52.25	1b	Skell
4	SE403674	River Tutt	43.75	1b	Skell

Table 8 *Tributaries on the River Ure - River Ouse (catchment area ≥20 km²) with their NRA classifications and matched WQ sites.*

Ungauged number	Grid Ref.	Trib name	Area (km²)	NRA classification	Matched WQS
1	SE508602	River Kyle	168.25	2	Kyle
Skelton	SE568554	River Ouse	3315.00	1b	Skelton

3.2.3 Effluent and Abstraction values

This Section reports on the monitored sewage and trade effluent that are required to be explicitly incorporated into the modelling of the Ouse system. There are 11 major sewage and trade discharges that require consideration, of which eight are sewage works, two are fish farms and one is a trade discharge. Table 9 documents the range of determinand values measured (usually ammonium, nitrate, BOD and pH on a monthly basis) in 1990 for these discharges.

Calculation of the total load to the river system requires knowledge of the actual outflows, however in this work only consent values were available. The calculations of the load into the model are thus approximate, but it is usual that over a year the average flow-rate is similar to the consent value. A comparison of the actual measured determinands with their consent values also shows that a proportion of the effluent sources exceed them in 1990, at least for part of the year.

The River Nidd, is greatly influenced by the effluent from Harrogate (north and south), a town of about 80,000, and nearby Knaresborough. This is especially so during summer when flows are low (less than 0.5 cumec at Gouthwaite) and the effluent is a significant proportion of the river flow. The headwaters of the River Swale suffer from effluent input from Richmond and the army base at Catterick (flows during the summer of 1990 did not drop below 0.8 cumecs at Richmond), as well as downstream from Cod Beck and the River Wiske. The River Ure also has a substantial effluent input from the WPC works at Ripon and a very large BOD concentration (at a low discharge) from the food factory WCF foods Ltd. The Ure, however, is a larger river than the others and can better assimilate the effluent.

Most of the major effluent points documented in Table 9 are incorporated in QUASAR as direct effluent inputs using measured values rather than consent values for WQ. In order to achieve a daily variation the measured concentrations are linearly interpolated to establish a daily time series.

The use of consent values for the flows bring associated errors in the input loads to the model. This error cannot be accounted for because of the lack of measurements. The sparsity of the WQ measurements also introduces load errors since they are used to attain a daily data set, but no actual knowledge of inputs between measurements is yet available.

QUASAR also requires that the full set of determinands are input for each effluent input. In the cases where measurements are not available realistic values are used as defaults. Table 10 shows the default set of determinands used in this modelling exercise. These are taken to represent a typical effluent discharge from a STW or WPC works. A comparison of these default values with the range of measured determinands in Table 9 identifies that they are realistic, although pH default values are perhaps high. This lack of monitoring introduces load errors into the modelling.

Table 9 *The range of determinand values for the main effluent points used as input in QUASAR, numbered down from the headwater stations. Also included are major effluent points on tributaries which are implicitly included in the tributary inputs.*

No from headwater	Name	BOD (mg/l)	Ammonium (mg/l)	Nitrate (mg/l)	pH	Consent flow (cumecs)
Swale						
1	Richmond WPC	4 - 24	3 - 13	-	6.8 - 7.4	0.029
2	Colbum WPC	12 - 37	0.1 - 28	-	7.1 - 7.5	0.051
3†	Thirsk STW	14 - 40	0.4 - 6.4	-	7.0 - 7.6	0.020
Nidd						
1	Glasshouses - Trout Farm	0.5 - 3.4	0.1 - 0.3	0.2 - 1.3	6.7 - 7.7	0.208
2	Low Laithe - Trout Farm	0.8 - 3.0	0.2 -0.6	0.4 - 1.6	6.3 - 7.3	0.251
3	Killinghall WPC	11.6 -18.4	0.9 - 3.7	-	7.0 - 7.3	0.013
4	Harrogate STW (N) - into Oak Beck	6.8 - 62.0	2 - 16.5	-	6.9 - 7.4	0.137
5	Knaresborough WPC	9 - 20	2.6 - 5.8	-	6.7 - 7.3	0.041
6†	Harrogate STW (S) -into Crimple Beck	7 - 15	3 - 10	-	7.0 - 7.4	0.137
Ure						
1	Masham WPC	50-240	6-35	-	6.8 - 7.4	0.003
2	Ripon WPC	4 - 14	2 - 22	-	7.3 - 7.7	0.165
3	WCF Foods Ltd	60 - 3800	0.3 - 2.5	0.2-1.0	6.6 - 7.2	0.003
4	Boroughbridge WPC	11 - 27	2 - 11	-	7.1 - 7.5	0.016

† means these effluent inputs are accounted for in the modelling by the monitored tributary values.

Table 10 *Default chemical inputs used for the effluent points eg. sewage treatment works.*

NO_3 (mg/l)	Cl (mg/l)	DO (mg/l)	BOD (mg/l)	NH_4 (mg/l)	Temp (°C)	pH
15.0	80.0	6.0	25.0	2.0	+2†	8.0

† means that the monthly STW discharge temperature equals the river temperature plus 2°C.

The major abstractions incorporated in this work are noted in Table 11, with the available consent values used in the modelling. Abstractions are taken mainly from the River Nidd and cause pollution problems at low flow during the summer at Knaresborough WPC. There is only one other major abstraction in the Ouse catchment at Catterick on the River Swale.

Table 11 *Consent abstraction values, numbered down from the headwater station*

No from headwater	Name	Abstraction (cumecs)
Swale		
1	Catterick - Army Camp	0.05
Nidd		
1	Glasshouse - Trout Farm	0.23
2	Low Laithe - Trout Farm	0.26
3	Knaresborough	0.23
4	Yorkshire Water	1.15

3.2.4 Algal inputs

Following measurements made on the Ouse (Marker et al., 1994), an approximate gaussian distribution with a maximum in July-August was assumed (see Figure 7) for the initial headwater points in the network and for the tributaries of the Ouse. This distribution is used as a substitute for algal growth in the model.

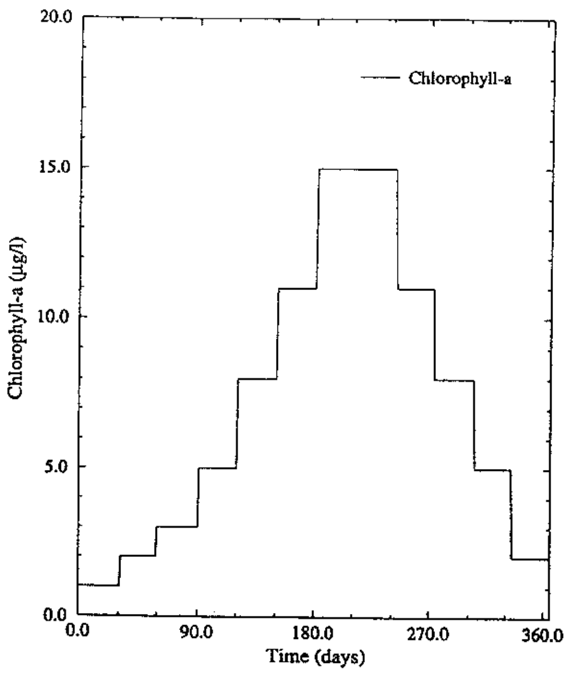


Figure 7 Chlorophyll-a distribution assumed in the model

4 Calibration Procedure

4.1 OBJECTIVE FUNCTIONS

The choice of an objective function with which to compare prediction with observation depends to some extent upon the nature of the data. In this work the goodness of fit was based partly upon minimising the efficiency factor E given by

$$E = 1 - \frac{\sigma_r^2}{\sigma_o^2}, \tag{2}$$

where $\sigma^2_r = \sum(p_i - o_i)^2/N$ and $\sigma^2_0 = \sum(\bar{o}_i - o_i)^2/N$ are the variance of the residuals and the observed determinands, respectively. In these expressions p_i is the i^{th} prediction, o_i the i^{th} observation of a total of N observations and $\bar{o}$ is the mean observed value. As a subsidiary goodness of fit estimate the chi-squared per point statistic χ^2_{pp} is also calculated ie.

$$\chi^2_{pp} = \sum_{i=1}^{N} \frac{(p_i - o_i)^2}{p_i\,(N-1)}\,. \tag{3}$$

These expressions show a basic reliance on the square of the errors weighted by some factor ($1/\sigma^2_o$ or $1/p_i$). Minimizing these functions produces a calibration aimed at a general fit to the data and not at fitting data extremes e.g. large peaks etc. However, in using these statistics to determine the goodness of fit, consideration has to be given to whether the overall pattern of the predictions matches the observations. This introduces a subjective criteria into the fit procedure and in some cases this priority has led to slightly different parameters being chosen to those that give a minimum in the described objective functions.

4.2 VELOCITY DISCHARGE RELATIONSHIPS

The QUASAR velocity-discharge relationships (v,Q) determine the time constant for each reach (see Appendix 1), which dictates the amount of time allowed for chemistry to take place in that reach. For each river this relationship has been found using a simple relationship between stage, discharge and cross-section area. This type of analysis was carried out for the NRA gauging stations where cross-sections were available. Widths and depths of the main rivers were also estimated using average cross-sectional values at these gauging stations, and a basic straight line interpolation was made between stations so that the widths and depths increase with distance down the river. Table 12 gives the results of this work, in which the expression $v = bQ^c$ was fitted to the calculated values, with v the water velocity (m s^{-1}), Q the discharge (cumecs) and b and c empirical parameters.

Table 12 *Quasar velocity-discharge relationship and average width and depth of the main rivers. The station types refer to velocity area (VA) or broad-crested weir (B).*

River and Gauging station	Station type	Av width (m)	Av depth (m)	b	c
Swale at Richmond - 27024	VA	30	2.75	0.0494	0.6960
Nidd at Birstwith - 27053	VA	20	1.50	0.0482	0.8226
Nidd at Hunsingore - 27001	B	50	4.50	0.0287	0.8483
Ure at Kilgram Bridge - 27034	VA	35	4.00	0.0583	0.7272
Ouse at Skelton - 27009	VA	75	7.50	0.0125	0.7927

4.2.1 Dynamic Water Balance of the Ouse System

QUASAR was applied to the Ouse catchment for the complete year 1990. Including the gauged headwaters and tributaries and the ungauged tributaries mentioned in Section 2.3, and using the methods outlined in Section 3.1, a good approximation to the inflows was achieved. The efficiency factor E was used to compare the QUASAR flow estimates with observations at the major NRA gauging stations at the downstream points on each river and at the furthest downstream point in the system at Skelton. The values of E shown in Table 13 identify the fact that the QUASAR flow estimates for 1990 agree very well with the gauging station observations on the River Nidd and on the River Ure. The agreement on the River Swale is good but it should be noted that the headwater inputs to this river were also simulated using the TM, as the gauging station was discontinued in 1980. Flows at York are fairly well described. Consequently the flows estimates in this simulation are expected to be reasonably reliable and a good approximation to the dynamic water balance of the Ouse system above York is expected to be achieved.

Table 13 *Comparison of the QUASAR estimates of flow for 1990 at certain reaches in the Ouse system with gauging station flows. The flow at Richmond on the River Swale was calculated using the TM.*

River (Station)	E(%)
Swale (27071)	70.7
Nidd (27001)	86.2
Ure (27007)	92.0
Ouse (27009)	68.8

4.3 WATER QUALITY CALIBRATION

The basic mass balance differential equations describing the variation of the water quality determinands are given in Appendix 1. In these equations the rate coefficients determining the transformation rates within each reach are obtained in general by calibrating the model moving downstream from one NRA WQ site to the next. However, in some cases, a stretch of river which has similar chemical and biological characteristics in all reaches is used to calibrate the model. The manner of calibration is sequential eg. the River Swale is calibrate in a sequential manner using firstly the WQ site at Catterick bridge, followed by calibrating the river stretch from Catterick down to Morton-on-Swale and then calibrating the stretch down to Thornton Bridge.

In the calibration exercise, rate coefficients are varied to produce good fits with data. The order in which these coefficients are calibrated can produce quite different sets of parameters. The calibration scheme suggested in Williams (1994) has been followed here. Table 14 lists the calibrated coefficients for the stretches of river on the River Swale and the River Nidd and Table 15 lists the calibrated coefficients determined for the river stretches on the River Ure and the River Ouse.

Table 14 *Rate coefficients used in the simulations for each length of main river on the rivers Swale and Nidd. Each length is identified by the WQ site used to calibrate the model.*

Rate coefficient (day^{-1})	**Swale - Catterick Bridge (9.3 km)**	**Swale - Morton-on-Swale (28.1 km)**	**Swale - Thornton Bridge (61.6 km)**	**Nidd - Killingham (19.6 km)**	**Nidd - Scotton Mill weir (25.6 km)**	**Nidd - Skip Bridge (57.5 km)**
Denitrification	0.04	0.04	0.04	0.02	0.15	0.02
BOD decay	0.07	0.07	0.10	0.04	0.06	0.10
Nitrification	1.10	0.30	0.10	0.20	0.40	0.30
O_2 - Sediment	0.05	0.05	0.10	0.08	0.06	0.05
BOD - Algae	0.10	0.10	0.10	0.02	0.10	0.05
Photo. O_2 <50µg/l	0.04	0.04	0.04	0.04	0.07	0.09
Photo. O_2 >50µg/l	0.01	0.01	0.01	0.02	0.02	0.02
BOD - Sed.	0.08	0.08	0.08	0.02	0.10	0.05
Algae Resp.	0.14	0.14	0.14	0.14	0.14	0.14
Algae Resp. Slope	0.013	0.013	0.013	0.013	0.013	0.013

Table 15 *Rate coefficients used in the simulations for each length of main river on the rivers Ure and Ouse. Each length is identified by the WQ site used to calibrate the model.*

Rate coefficient (day^{-1})	Ure - Ripon STW (30.5 km)	Ure - Borough-bridge (40.0 km)	Ouse - Aldwark Bridge (49.8 km)	Ouse - Skelton (59.1 km)
Denitrification	0.05	0.05	0.05	0.05
BOD decay	0.08	0.10	0.15	0.15
Nitrification	0.10	1.10	0.20	0.20
O_2 - Sediment	0.10	0.07	0.10	0.10
BOD - Algae	0.07	0.07	0.07	0.07
Photo. O_2 <50µg/l	0.04	0.07	0.04	0.04
Photo. O_2 >50µg/l	0.01	0.01	0.01	0.01
BOD - Sed.	0.08	0.08	0.10	0.10
Algae Resp.	0.14	0.14	0.14	0.14
Algae Resp. Slope	0.013	0.013	0.013	0.013

The rate coefficients attained in the calibration exercise are mainly within the limits reported in Appendix 1 for each coefficient. However it is evident that there is a significant variation between the calibrated rate coefficients required for stretches of river with input effluent sources and those without any major anthropogenic sources. For example, those stretches of river with large inputs of ammonium from effluent sources generally require high nitrification rates, possibly high denitrification rates and significant oxygen production through photosynthesis. These rates occasionally exceed those recommended as upper limits in Appendix 1 by a factor of two. It is however certainly possible that very large reaction rates occur in waters suffering large excesses of nutrients where high microbiological activity is present. The EPA document by Bowie et al. (1985) can also be referred to for acceptable values for these rate constants, and these do give slightly wider limits than those in Appendix 1 (taken from Williams, 1994). A comparison of the acceptable rate coefficients is given in Table 16.

Table 16 *Comparison of acceptable rate coefficients*

Rate coefficient (day^{-1})	Williams (1994)	EPA (1985)
Denitrification	0.00 - 050	0.02 - 1.00
BOD decay	0.00 - 2.00	0.01 - 3.37
Nitrification	0.01 - 0.50	0.03 - 3.90
O_2 - Sediment	0.00 - 0.50	0.01 - 3.00
BOD - Algae	0.00 - 0.50	-
Photo. O_2 <50µg/l	0.00 - 0.03	0.00 - 0.08
Photo. O_2 >50µg/l	0.00 - 0.02	-
BOD - Sed.	0.00 - 2.00	-
Algae Resp.	0.14	-
Algae Resp. Slope	0.013	-

5 Discussion of Results from Calibration Exercise

The QUASAR predictions of WQ in 1990 at various reaches corresponding to measured NRA spot samples for each main river in the Ouse catchment are shown in Figures 8 to 32. These figures are the results of the calibration procedure outlined in Section 4.3, in which three calibration WQ sites were used for the rivers Swale and Nidd and two calibration WQ sites for the rivers Ure and Ouse. The figures for each site are arranged so that the top four diagrams show the conservative modelled determinands; flow, temperature, chloride and pH and the bottom four show the non-conservative determinands; biological oxygen demand (BOD), nitrate, dissolved oxygen (DO) and ammonium. The calibration results of each main river system will be described separately

5.1 RIVER SWALE

Figure 8 shows the predictions of the output of reach 1 together with observations at Richmond WQ site. This initial set of diagrams should not be considered a comparison of predicted results with observations because the observed data at Richmond are actually the initial measurements interpolated and used as input to the Swale. The fact that the first reach is only 2.9 km from the initial point in the network and that there are no other inputs to the reach explains why the two sets of data are similar.

The river above Richmond has an NRA classification of 1a, indicating that the water is considered to be of high quality. This can be concluded from the observations shown in Figure 8, where nitrate levels are less than 1 mg/l and ammonium concentrations less than 0.1 mg/l. BOD concentrations are less than 2.5 mg/l and have a periodic pattern. An increase in BOD is seen starting in spring and lasting through to the early summer months. This is probably due to the death of algae (eg. diatoms and green-algae) during this period. A second increase in BOD is seen in autumn - possibly due to washing in of organic matter. DO has the usual behaviour, decreasing during the summer months due to a lower saturated oxygen content and a reduced reaeration rate brought about by low flows.

Observations at Catterick Bridge were used to calibrate the model reach parameters for the stretch of river down from the initial point at Richmond. Figure 9 shows that the conservative determinand predictions closely follow observations, although the flow comparisons are misleading since the observed flow in this case is that input at the headwater (which was also modelled).

The stretch of river from Richmond down to Catterick Bridge is influenced by the effluent load input from the residential WPC's at Richmond and Colburn. Combined, the two WPCs input a large amount of ammonium (annually ~20 mg/l at 0.05 cumecs) into the river. In order to reduce the ammonium predictions at Catterick Bridge to a reasonable level (although still high during the summer) a large nitrification rate of 1.10 day^{-1} was required in the model calibration for this stretch of river. Although this is a relatively large rate, it is possible that the river conditions are such that nitrosomas bacteria concentrations are high directly downstream of the effluent inputs, thereby leading to large nitrification rates. This nitrification rate was not deemed to be totally unrealistic because of this possibility. Figure 9 shows that both nitrate and DO predictions compare reasonably well with observations, with the DO predictions dropping below the observations during summer due to the large nitrogenous oxygen demand in the model. The BOD predictions compare reasonably well with observations and generally the observations are higher in value than those at Richmond due to the inputs from the WPCs. The BOD decay rate coefficient required to fit the data is quite low (0.07 day^{-1}). indicating that organic matter in the upper Swale has a relatively constant degradation rate.

Generally the predictions of the conservative determinands compare well with observations at the downstream sites of Morton-on-Swale (Figure 10), Topcliffe Bridge (Figure 11) and Thornton Bridge (Figure 12). The predictions of pH at these sites are slightly lower than observations during the spring and summer months. Peaks in the chloride concentration predictions during the wet months coincide with those observed, although during the summer months the chloride predictions are lower than observed. These peaks are basically due to the varying inputs from the tributaries. Temperature predictions are truncated during the summer months which follows the headwater inputs, used predominantly as the inputs for the ungauged tributaries. A comparison of predicted and observed flows is not valid for Morton-on-Swale and Topcliffe Bridge since the observed flows shown in these figures are actually those estimated for Richmond and measured at Crakehill respectively. The predicted flow at Thornton Bridge compares well with observation at Crakehill with an efficiency factor of 71%, although the predicted falling limb of the hydrograph drops more quickly than is observed.

Figures 10, 11 and 12 show the predictions of the non-conservative determinands at the three sites. In progressing down the river system from Catterick Bridge to Morton-on-Swale the predicted ammonium concentrations decrease due to dilution from tributaries and a nitrification rate of 0.3 day^{-1} produced a reasonable fit with observation. A corresponding increase in the predicted nitrate concentrations at Morton-on-Swale is not evident since the total nitrification transfomation rate is low (this rate is proportional to the ammonium concentration which is generally less than 0.4 mg/l and the rate coefficient). In moving down the river to Thornton Bridge a lower nitrification rate of 0.1 day^{-1} is required. Both the predicted ammonium and nitrate concentrations increase down the river system from Morton-on-Swale due to tributary and agricultural inputs and this is especially evident during the autumn and winter months when there are periods of high flow. It is gratifying to see that the observations also increase during high flows. Overall the nitrate predictions agree well with observations at all three sites, whereas the ammonium predictions agree well at the first two upstream sites but not at Thornton Bridge. This last fact however may be explained by the input of transient non-point sources of ammonium (eg farm slurry) in the lower Swale region which is agriculture dominated.

The observations of BOD give evidence for a peak in April-May at Morton-on-Swale and at Topcliffe Bridge, whereas at Thornton Bridge a larger number of observations were made and the early summer peak pattern is not so clear with a possible additional peak during June being displayed. The predicted BOD behaviour at the three sites during the spring-summer months is strikingly different to that observed. A peak in the predicted BOD is evident during July-August which can be explained by the monthly chlorophyll-a concentration distribution assumed in this work. The predicted BOD peak can be explained by the fact that the algal decay rate is proportional to the density of algae present, and in the process of algal decay oxygen is required. Thus an increase in BOD is evident when algal concentrations are large, as they are assumed to be in July-August. A more appropriate distribution for chlorophyll-a would seem to be one with a maximum during April-May. However no chlorophyll-a measurements have been made on the Swale by the NRA to support this. Generally the DO predictions of the three sites follow those of the observations, but during the summer months the predictions are lower than observations indicating that greater reaeration could be required in the model.

Figure 13 shows the non-conservative determinand predictions for each reach and the NRA observations taken at certain points along the Swale on one day during the summer and the winter of 1990. These plots allow the influence of STWs or tributary inputs on the main river to be discerned. Effluent from Catterick army camp (8.3 km from Richmond Bridge) causes a substantial increase in the ammonium concentration predicted during the summer with increases in nitrate and BOD. A corresponding decrease in DO predictions is evident, due to the large denitrification values required in the model. The observations also follow these patterns, although the ammonium observation is smaller than that predicted by about 50%. During the winter, less substantial increases in ammonium, nitrate and BOD is predicted with a lower predicted drop in DO. This difference is due to the dilution effect of the Swale, with the daily flow predicted to be 2.5 cumecs on July 3 and 7.9 cumecs on November 27 at Catterick. An increase in the nitrate predictions is also evident downstream of the input of Bedale Beck (at 30.3 km). Only a small increase in BOD and an even smaller increase in nitrate predictions is evident downstream of the input from the River Wiske (at 49.7 km). Downstream of Cod Beck (at 55.6 km) nitrate and ammonium predictions again increase but not as much as observations, suggesting that the biological processes need to be examined here in more detail. Throughout this region of the Swale, the predicted DO content consistently decreases. Generally the predictions agree with the observations, although the ammonium and summer nitrate observations are greater than those predicted for the Swale in the Vale of York.

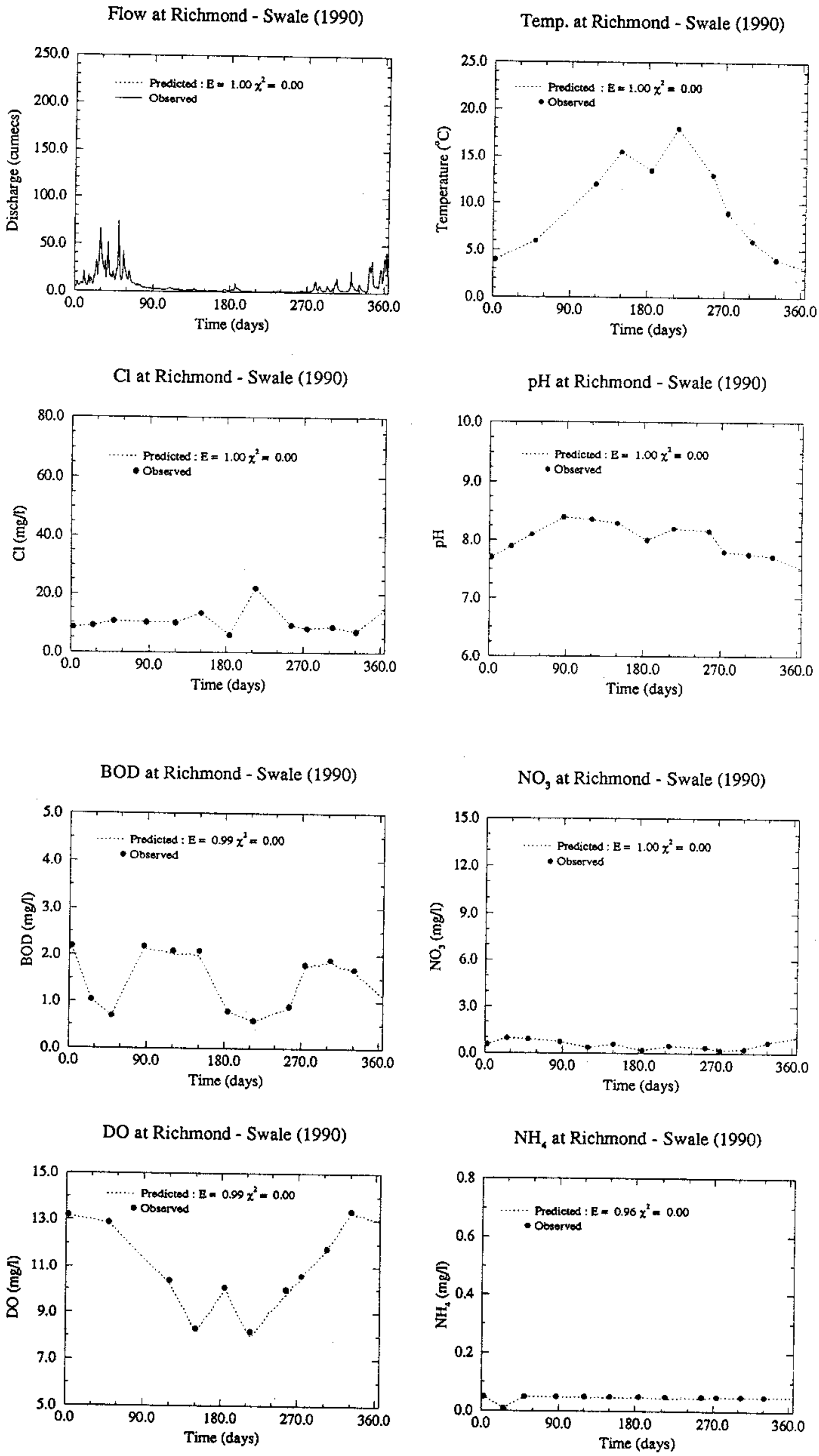


Figure 8 QUASAR predictions compared with NRA observations, Richmond - Swale (1990)

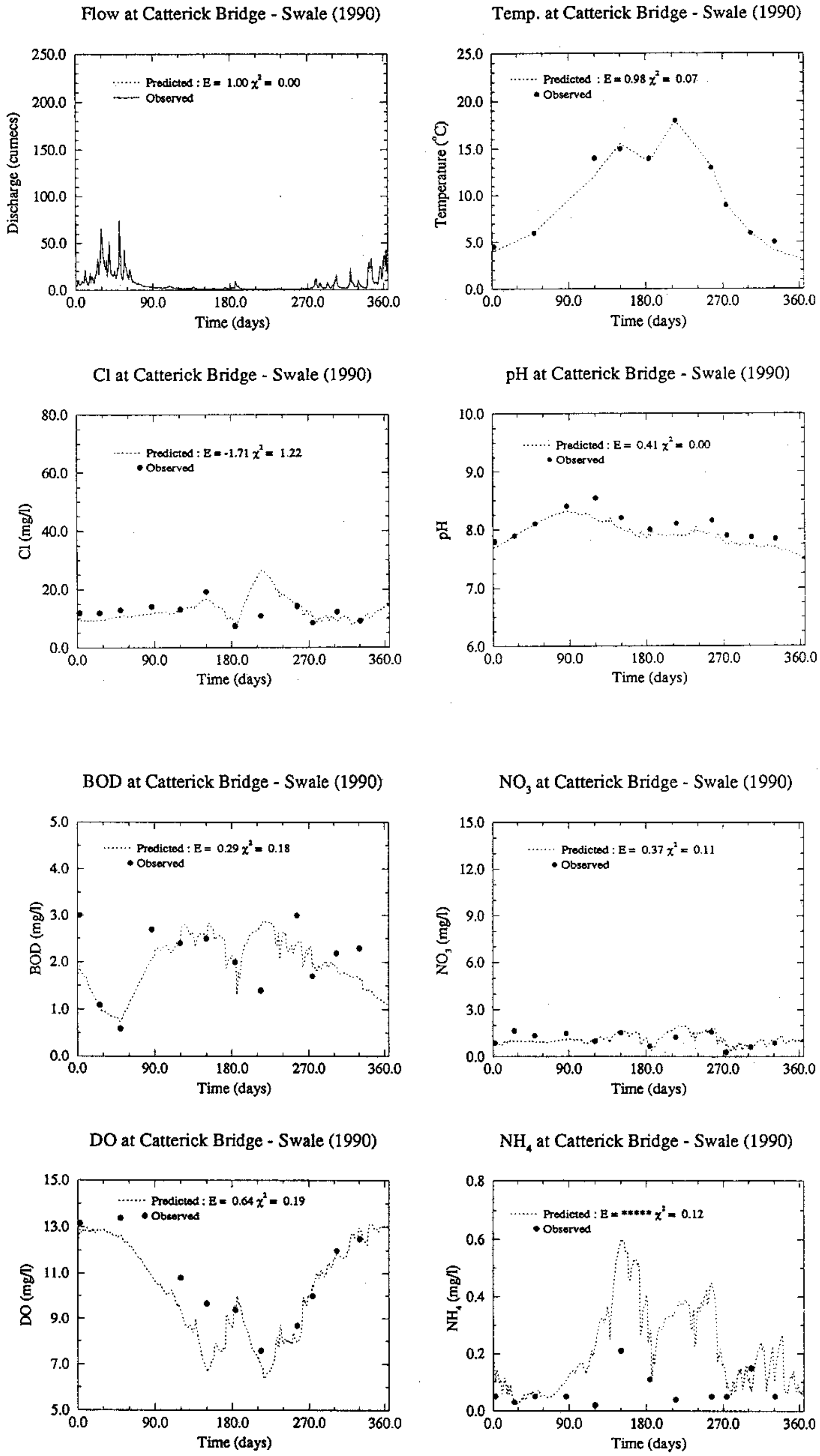


Figure 9 QUASAR predictions compared with NRA observations, Catterick Bridge - Swale (1990)

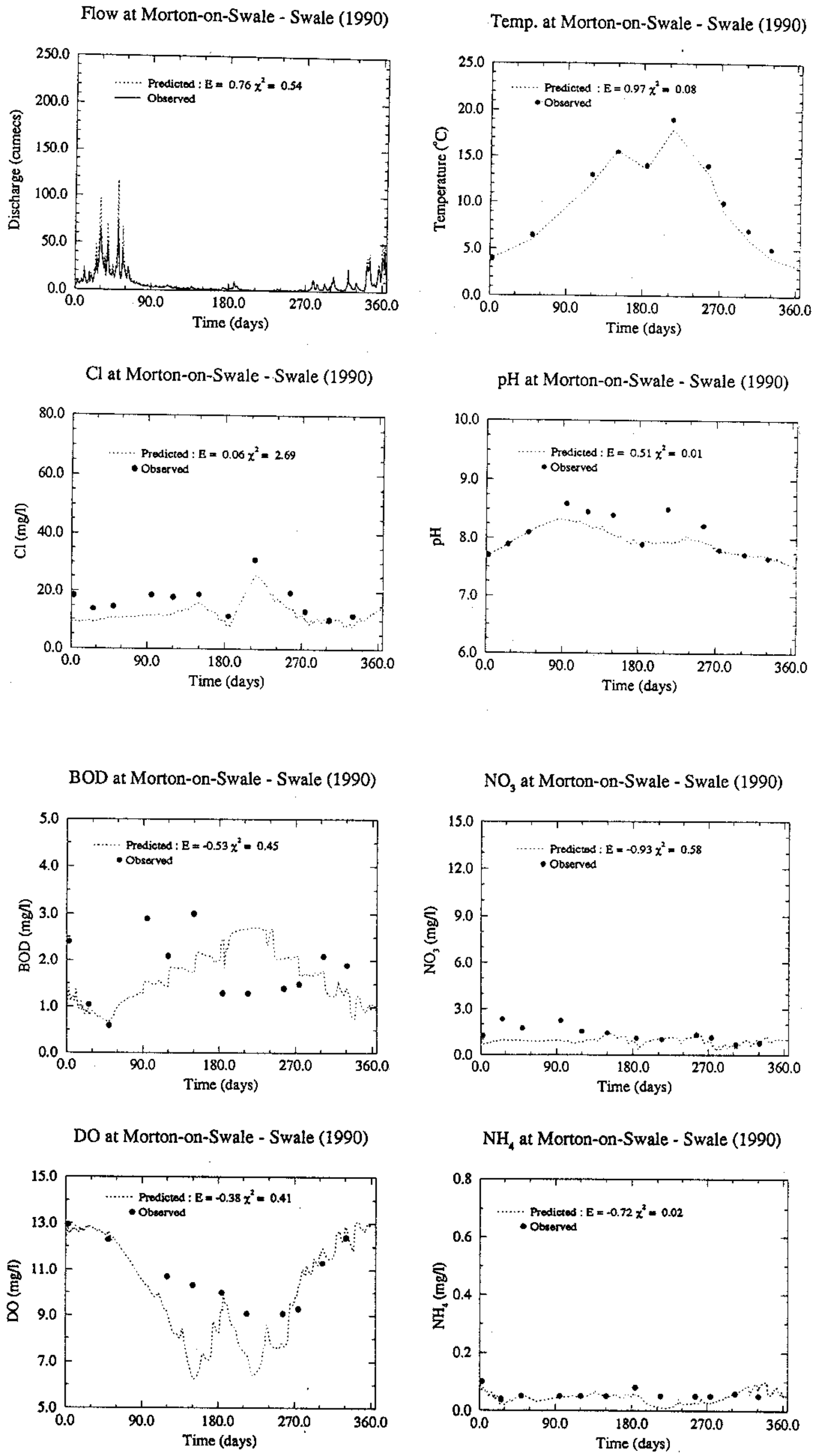


Figure 10 QUASAR predictions compared with NRA observations, Morton-on-Swale - Swale (1990)

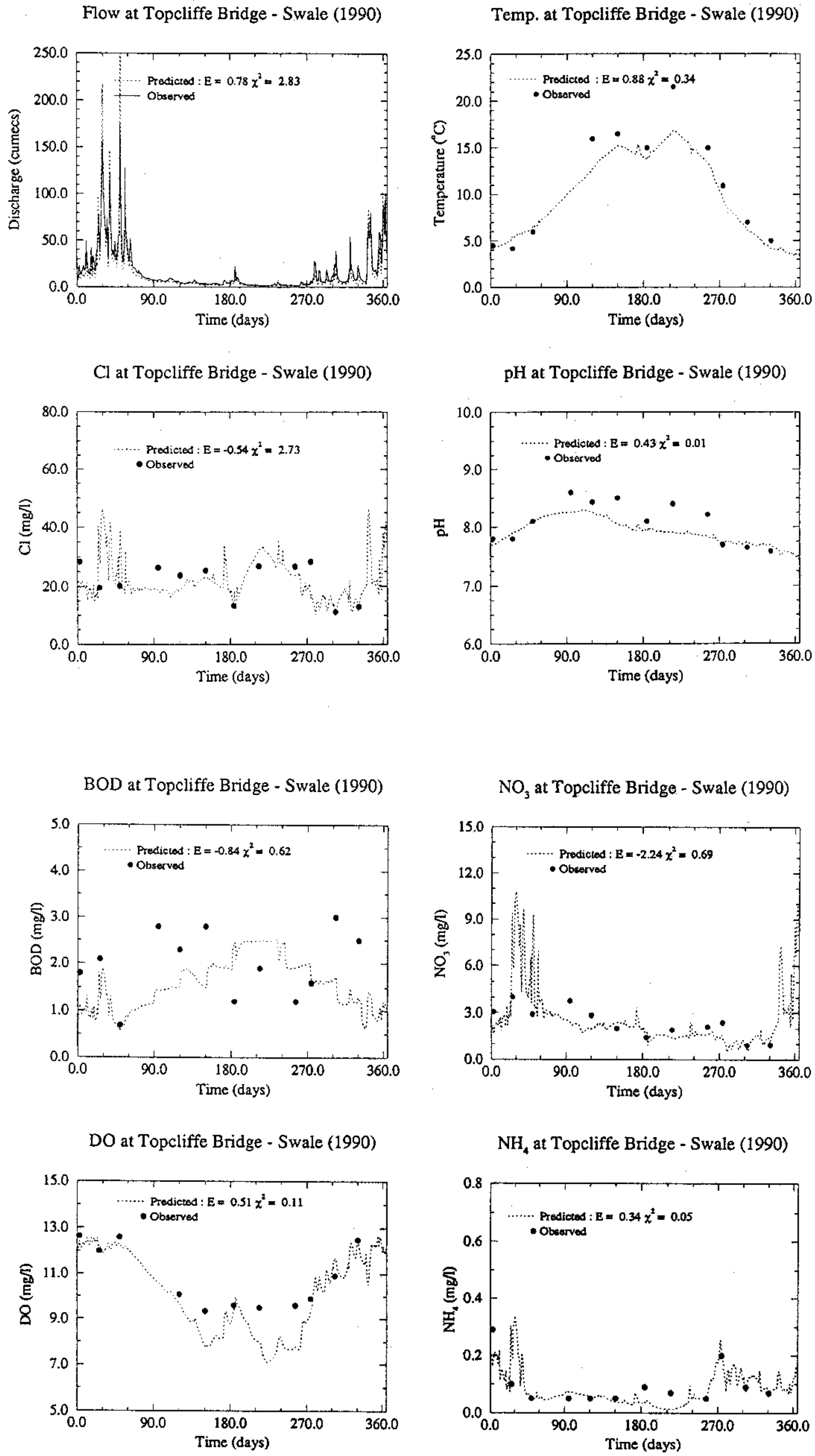


Figure 11 QUASAR predictions compared with NRA observations, Topcliffe Bridge - Swale (1990)

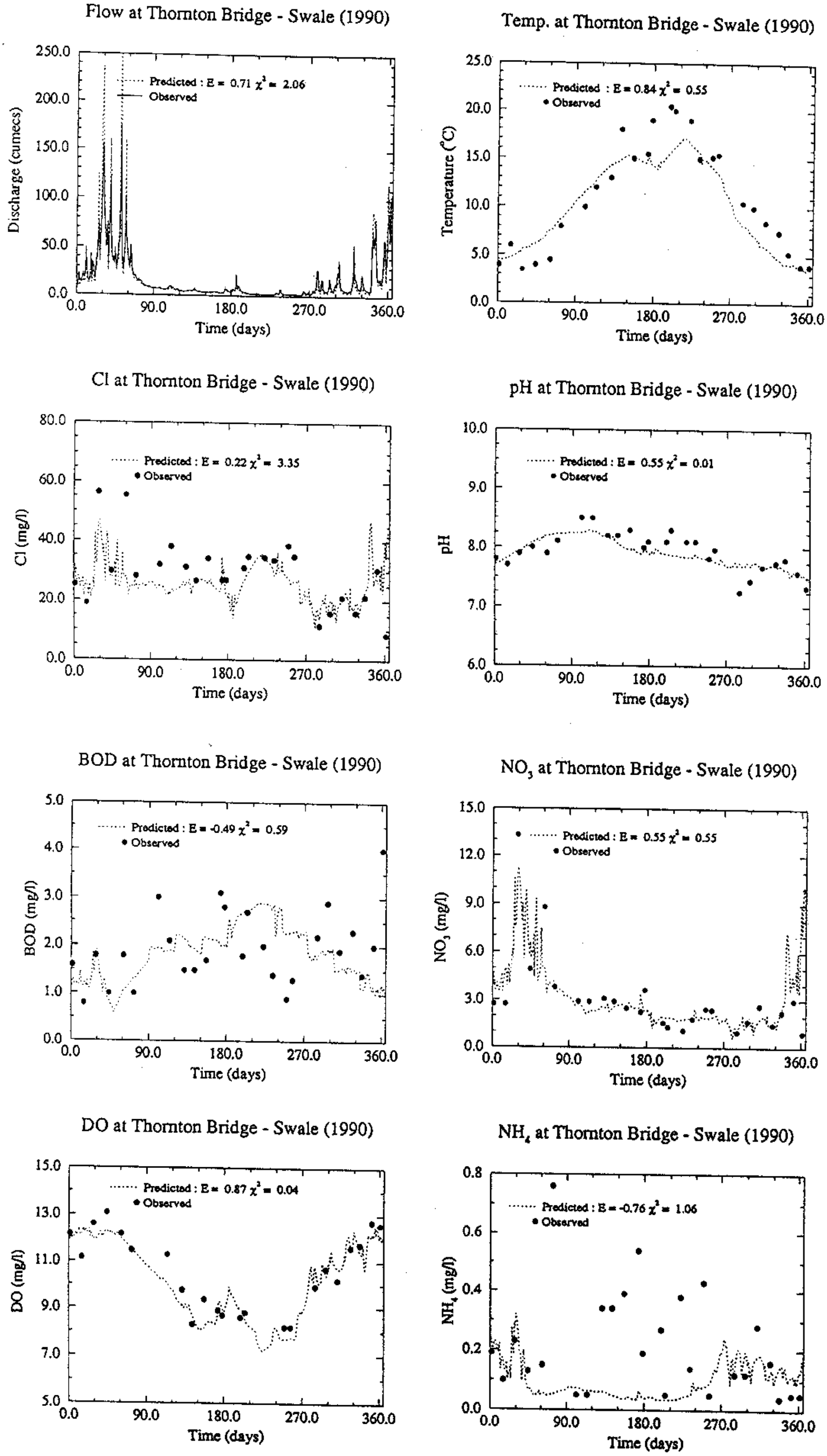


Figure 12 QUASAR predictions compared with NRA observations, Thornton Bridge - Swale (1990)

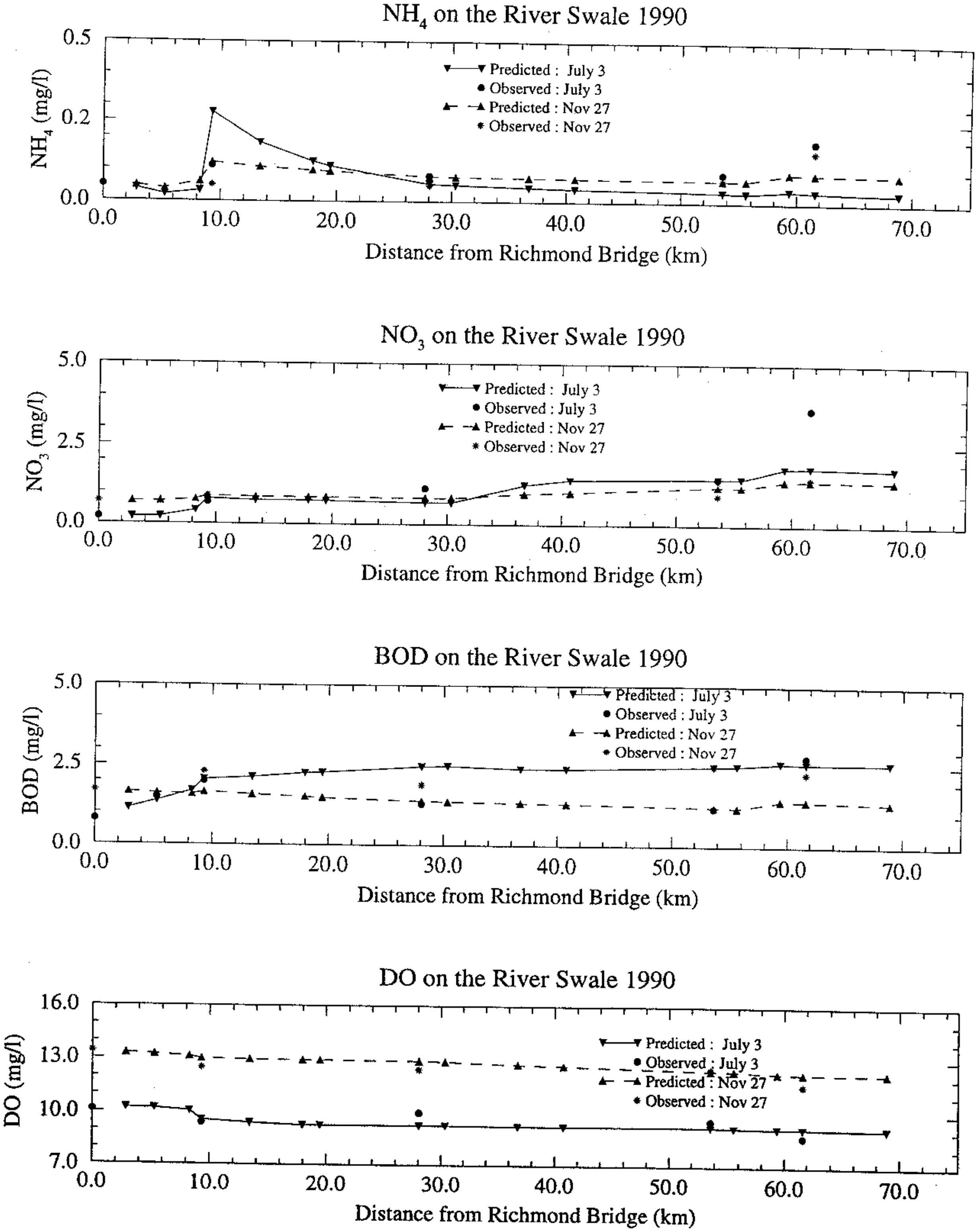


Figure 13 QUASAR predictions compared with NRA observations, along the River Swale on July 3 and November 27 (1990).

5.2 RIVER URE

Figures 14 to 17 show the comparison of predictions with observations for the River Ure. The first of these figures shows the predictions of the output of reach 1 in the Ure QUASAR network, and essentially shows the initial inputs to the Ure. The Ure and its tributaries throughout Wensleydale have an NRA classification of 1a and are relatively pollution free, as exemplified by the observations in Figure 14.

For this river, two calibration stretches were chosen rather than calibrating river stretches between WQ sites. The first stretch was taken to be from Kilgram Bridge to Ripon WPC works and the second stretch from Ripon WPC works to Boroughbridge. These stretches were chosen on the grounds of chemical similarity in terms of inputs and the WQ sites within the stretches used as the calibration points. The alternate procedure of calibrating river stretches between WQ sites caused significant problems, the major one being due to the effect on the river WQ at Hewick Bridge of Ripon STW which is only 1 km upstream. WQ at Hewick Bridge and throughout the lower stretch of river is significantly affected by the STW input and consequently this stretch requires consideration as a whole.

The WQ of the stretch of river from Kilgram Bridge to Ripon WPC works is represented by the WQ site at West Tanfield, shown in Figure 15. In this stretch of river the conservative determinands are well predicted, with good fits to the observations achieved (the observed flow is that at Gouthwaite). The ammonium predictions compare well with observation. Nitrate concentrations, however, are slightly underpredicted and this is difficult to account for in the model: increasing the nitrification and denitrification rate coefficients appropriately does not produce significant changes. It is likely that additional sources are required to produce good fits, and this region is an agricultural area where non-point agricultural sources are likely. BOD observations seem to show a peak in July/August, which is approximately simulated by the model since this is when the assumed algal distribution used also peaks, and generally the fit is reasonable throughout the year. Similarly DO predictions closely follow the observations.

Conservative determinand predictions at Hewick Bridge (Figure 16) and at Boroughbridge (Figure 17) follow the observations reasonably well, with only chloride concentrations at Hewick Bridge not producing a good fit during the spring/summer months. The flow at Boroughbridge is well described when compared to observations from the NRA gauging station at Westwick Lock with an efficiency factor of 92%. Ammonium predictions at Hewick Bridge are significantly greater (by a factor of four) than the observations during the dry months. This overprediction is due to the large amount of ammonium input from Ripon STW which in the model is unable to decay or dilute sufficiently in the 1 km reach from Ripon STW to the WQ site. At present ammonium in the model can only be decreased by increasing the nitrification rate, with a maximum quoted value for this rate of 0.5 day^{-1} (Appendix 1). In this calibration a higher rate of 1.1 day^{-1} has been used. It is of course possible that other factors are causing the ammonium to be removed eg. through biological means: algae consume ammonium thereby removing it from the river system. At present no explicit biological linkages are modelled within QUASAR. The nitrate predictions by comparison describe the observations reasonably well, with the calibration of two parameters. As a consequence of using high nitrification rates, DO predictions also drop below the observations during low flow conditions when reaeration is low. The BOD observations generally have the same pattern as in the other rivers but with the spring-summer peak moving into mid-summer. For this reason the BOD predictions are good since the chlorophyll-a distribution used in the model peaks in the summer.

Boroughbridge is approximately 10 km downstream of Hewick Bridge and during this distance the high predicted ammonium concentrations are diluted and transformed to the level shown in Figure 17. These concentrations are however still slightly larger than the observations. Nitrate is again well predicted by the model, as is DO, although there is a shortage of observation points during the summer to definitely conclude this. There is a large input of BOD from WCF foods Ltd in this stretch of river (see Table 9), but this input is assimilated due to the combined BOD decay rate of 0.1 day^{-1} and the relatively large dilution effect of the river (low flow is greater than 1 cumec at Boroughbridge). Overall BOD is predicted reasonably well, with a strong mid-summer peak which is also evident in the observations

Figure 18 shows the non-conservative determinand predictions for each reach and the NRA observations taken at certain points along the Ure on June 25 and November 26, 1990. On these days the predicted flows out of the first QUASAR reach are 0.4 and 1.5 cumecs for summer and winter, respectively. The upper section of the Ure is relatively pollution free with only a small effluent load from Masham STW (at 8.4 km from Kilgram Bridge). A substantial increase in the ammonium and nitrate predictions and a small increase in BOD is evident downstream of Ripon STW (at 30.0 km). These inputs result in a corresponding decrease in the DO predictions, where oxygen is required to convert the large ammonium inputs from the STW to nitrate. A further increase in the BOD predictions is also evident downstream of the effluent input from WCF Ltd (at 38.1 km). Generally the predictions follow the observations but it is also noticable that the winter predictions are slightly closer to the observations than are the summer predictions. The nitrate observations below the input from the Skell and Laver (at 29.5 km) are also greater than those predicted by a factor of 2.

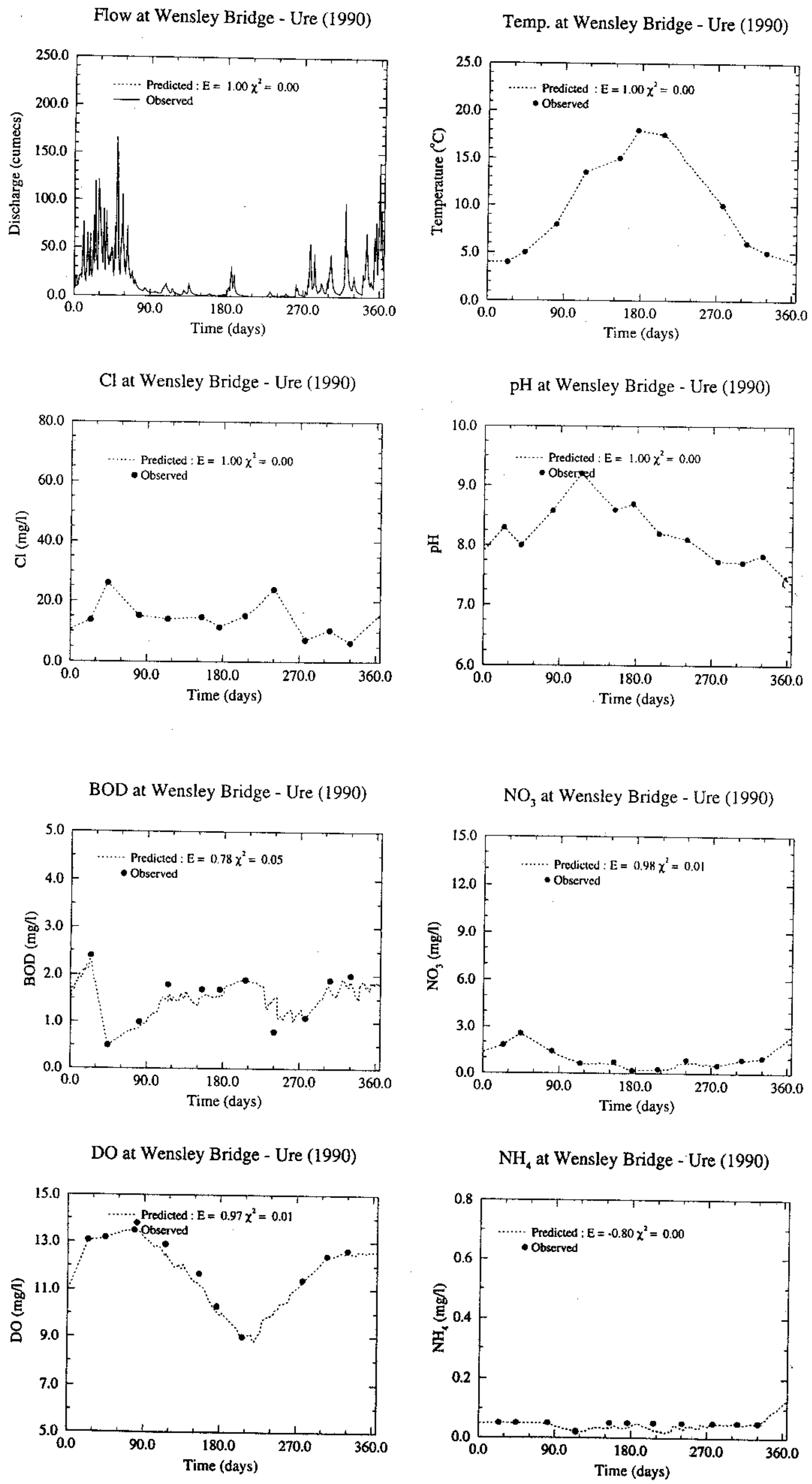


Figure 14 QUASAR predictions compared with NRA observations, Wensley Bridge - Ure (1990).

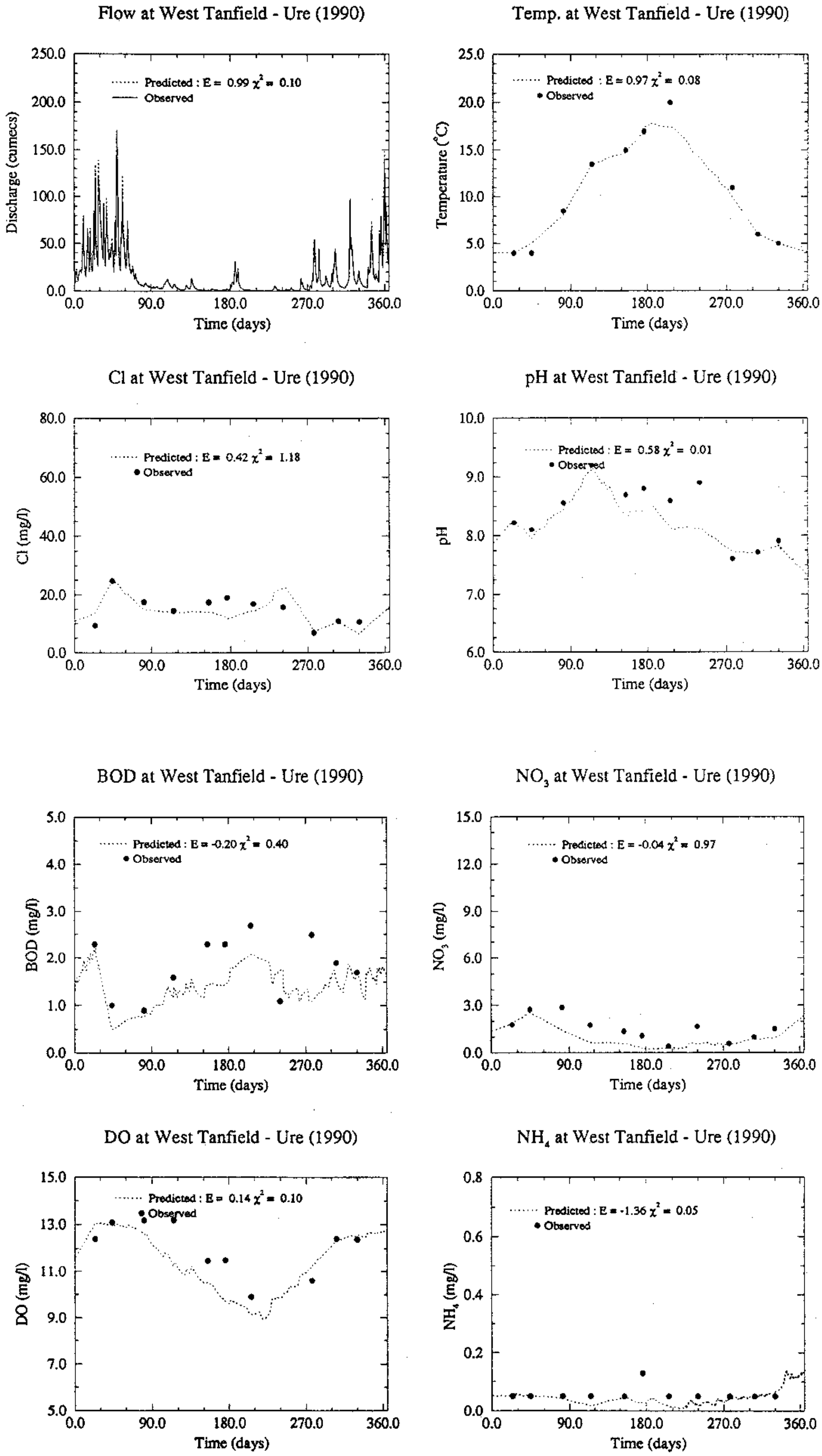


Figure 15 QUASAR predictions compared with NRA observations, West Tanfield - Ure (1990)

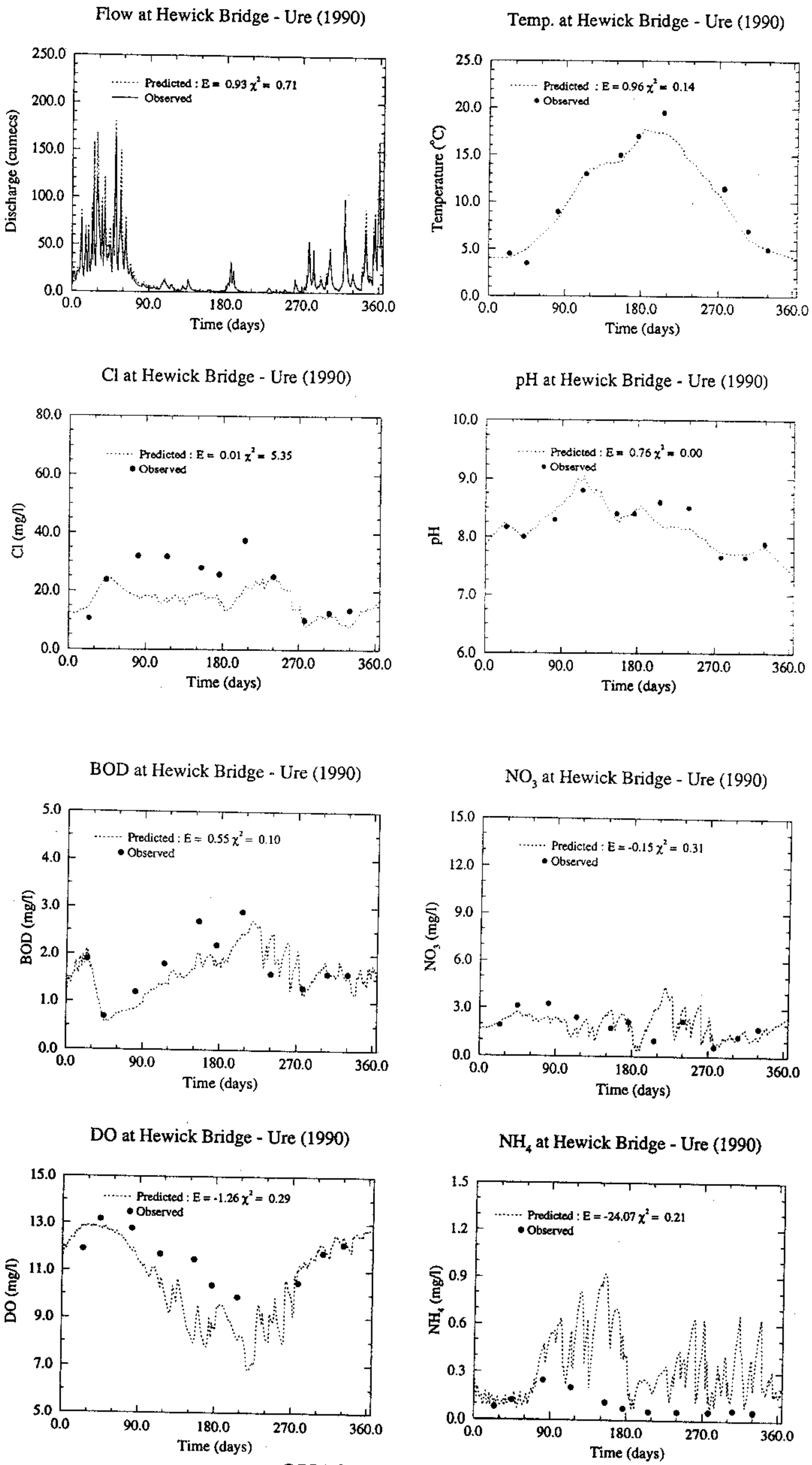


Figure 16 QUASAR predictions compared with NRA observations, Hewick Bridge - Ure (1990)

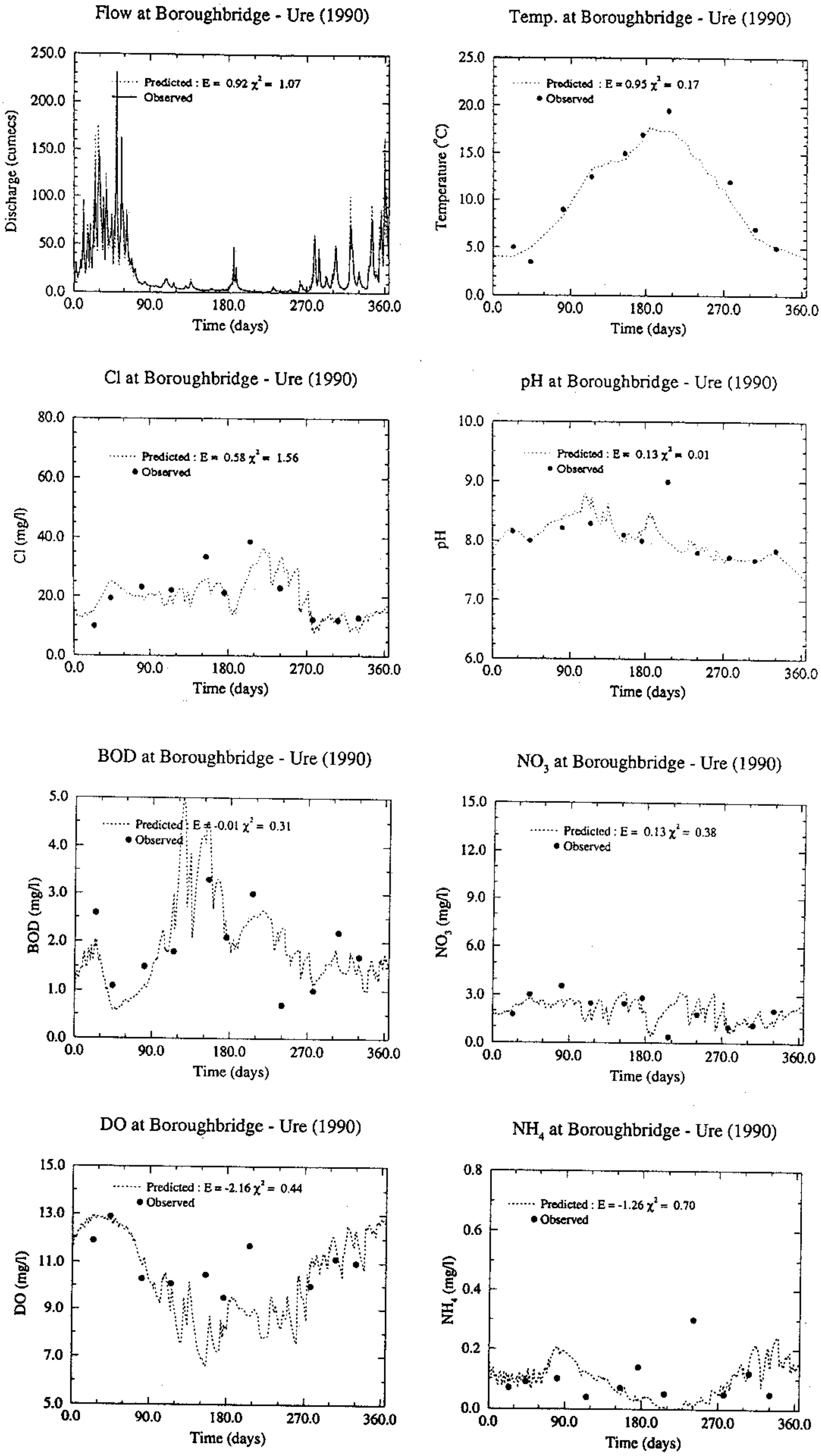


Figure 17 QUASAR predictions compared with NRA observations, Boroughbridge - Ure (1990)

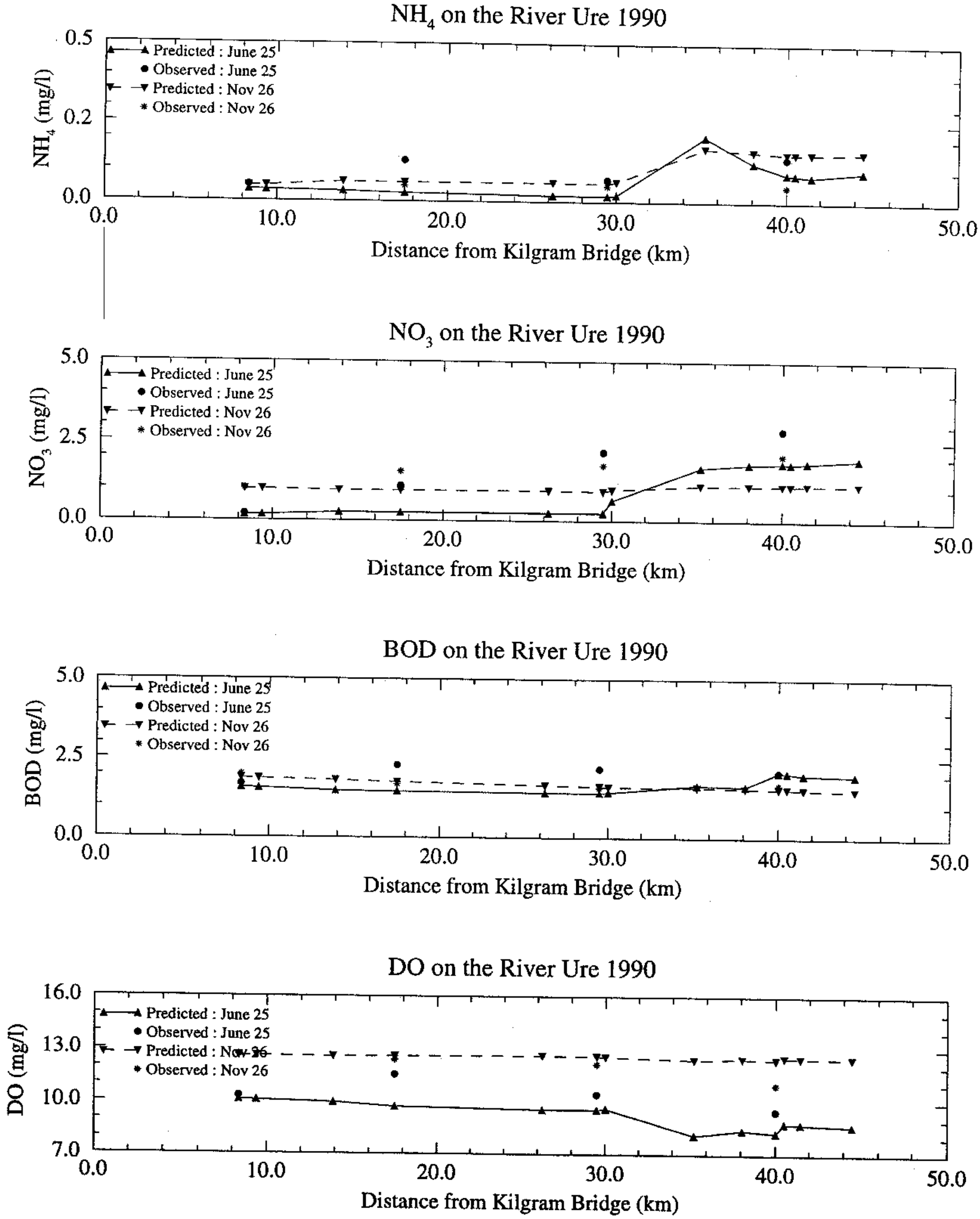


Figure 18 QUASAR predictions compared with NRA observations, along the River Ure on June 25 and November 26 (1990).

5.3 RIVER NIDD

Figures 19 to 29 show the predictions of the eight QUASAR determinands versus observation for all 11 WQ sites on the River Nidd. Initially calibration was carried out on the stretch of river from the initial starting point in the network at Gouthwaite reservoir to Killinghall (see Figures 19 to 24 for the calibration results). The figures show that conservative determinand predictions agree well with observations down to Low Laithe trout farm, however flow comparisons are again not valid since observations were only available at Gouthwaite. At the Killinghall WQ site the predicted conservative determinands chloride and pH are lower than those observed, possibly indicating missing inputs to QUASAR from other effluent sources or non-point sources.

The upper stretch of river is relatively pollution free with an NRA rating of 1a. The main effluent into this stretch arises from the Glasshouses Trout Farm (G. T. F.) and Low Laithe Trout Farm (L. L. T. F.). Both the ammonium and BOD predictions and observations increase in the Nidd below each of the fish farms, but the effect is more pronounced for the trout farm at Low Laithe. Pollution loads from these fisheries are however small and easily assimilated by the main river. Nitrate and ammonium concentration predictions at Killinghall are generally lower than observed. This feature cannot be explained by the transformation rates used; a moderate nitrification rate of 0.2 day^{-1} and small denitrification rate of 0.02 day^{-1} were used for this stretch of river. This perhaps indicates a lack of source inputs for the model. The BOD observed concentrations have no apparent pattern during the spring/summer months but are generally higher during the wet months, whereas predicted BOD has a peak during July-August due to the assumed chlorophyll-a distribution described previously. DO predictions agree well with observation.

Below Killinghall, large effluent loads are input into the river from Harrogate STW (North) and Knaresborough WPC. The stretch of river from Killinghall to Scotton Mill weir below these effluent sources was calibrated, with Figure 25 showing the predictions at the calibration point. In order to reduce the predicted ammonium concentrations to those corresponding to the observations at Scotton Mill weir a nitrification rate of 0.40 day^{-1} was applied in the model. This large rate coupled with the high ammonium concentrations results in a very large total nitrification rate which would cause DO to drop to zero during the summer months with significant problems downstream. However, during the summer-autumn months of 1990 (a drought year) in order to maintain the DO concentrations in the river for fish to survive, an amount of liquid oxygen (0.25 tonnes per day) was fed into the river above Harrogate STW. Including this input of oxygen as an effluent input into QUASAR the predictions shown in Figure 25 were achieved. At Scotton Mill weir the predicted DO concentrations agree well with observations during the wet months but are below those observed during the spring/summer months and have approximately the opposite behaviour to the ammonium concentrations. The ammonium and nitrate predictions closely match the observations. Since large quantities of BOD are also input into the river system no winter peaks or spring/summer algae pattern can be seen for the observed distribution at Scotton Mill weir.

Flow predictions at Scotton Mill weir compare well with the observations at the NRA gauging station at Birstwith Bridge, with an efficiency factor of 83%. The predictions of the conservative determinand chloride are generally greater than observed. pH predictions tend to be lower than those observed, and especially so during the spring and summer months. It is likely that the difference evident here is due to the two gauged WQ sites used as the major matching sites for inputs to the Nidd. The WQ site at Gouthwaite has an average pH over the year of approximately 7.1, whereas the site at Coppice beck has an average of approximately 7.6 which agrees with observations for the other tributaries and headwaters in the Ouse catchment. Gouthwaite is used as the matching site for six of the tributaries on the Nidd and including these inputs in the model results in lower predicted pH values at Skip Bridge than the average for the Ouse system. Water in Gouthwaite reservoir is more acidic than the surrounding tributaries for several reasons. There is likely to be a greater acidic input to Gouthwaite from the moorlands and this acidic water in the reservoir probably does not flush through the system as quickly as it would through a tributary. Longer residence times in reservoirs also probably allow significant ammonium nitrification and coupled with small denitrification rates (Whitehead, 1992) greater acidic conditions can be produced.

In QUASAR pH is modelled as a conservative quantity, but in reality it is greatly influenced by the changes in CO_2 concentration and the enhanced partial pressures of soil water CO_2 input into streams and rivers. In general, increasing temperature means greater CO_2 degassing of soil waters input into streams, resulting in generation of alkalinity (Hope et al., 1994). The in-river processes of respiration and photosynthesis by algae also affect CO_2 concentrations and this may give rise to the two peaks discernable in the pH observations downstream of Killinghall. The other major influence on the pH of a river is the lithology of the catchment and for the areas of the Ouse catchment considered, the underlying rock is Carboniferous limestone which will introduce substantial bicarbonate ions into solution thereby producing an alkaline water. It is also likely that acidifying effects occur in the main river due to the substantial inputs from STWs.

Figures 26 to 29 show the comparison of the predictions with observations for the remaining downstream stretch of river, which was calibrated using the observations at Skip Bridge (Figure 29). The predicted chloride concentrations for this river stretch tend to agree with observations during the wet months but are greater than those observed during the dry months. pH predictions are generally lower than observed for these WQ sites. The predicted temperature trend tends to follow the initial headwater inputs and agrees reasonably well with the observations, except for the peak where the predictions are truncated. An efficiency factor of 86% is achieved for the flows at Walshford Bridge which corresponds to the NRA gauging station at Hunsingore weir (again the predicted falling limb of the hydrograph drops more quickly than observation). The gauging station at Skip Bridge is unreliable at high flows (Lewis, 1994a) and the observed flow in Figure 29 is that for Hunsingore weir (5 km upstream) and the comparison of flows only approximate.

Ammonium concentrations in the upper parts of this stretch of river are overpredicted during the dry months, but generally agree well with observations at Walshford Bridge and Skip Bridge. The predicted nitrate patterns give a very good agreement with the observations, although the efficiency factors do not represent this. BOD concentrations are greatly influenced by the inputs from the STWs in the upper stretch of river and observations do not show any distinguishable pattern. This is contrasted with the lower stretch below Crimple Beck in which the observations display a distinct peak during the spring/summer algal bloom. The BOD predictions describe the observations poorly in this stretch of river. The DO observed concentrations have the usual pattern and this is generally well predicted by the model. However, initially at the top of this stretch and at Skip Bridge QUASAR does underpredict the observations during the spring/summer period possibly due to a lack of modelled algae in this period when it is likely that larger amounts of oxygen would be produced through photosynthesis.

Figure 30 shows the non-conservative determinand predictions for each reach and the NRA observations taken at certain points along the Nidd on June 21 and November 27, 1990 (the predicted flow from the first reach downstream of Kilgram Bridge was 2.3 and 20.8 cumecs respectively). The upper section of the Nidd is relatively pollution free with only a small effluent load from the trout farms at Glasshouses (at 4.9 km from Gouthwaite Reservoir) and at Low Laithe (at 7.7 km). These pristine conditions are altered dramatically downstream of the effluent input from Harrogate (N) (at 23.5 km), and in turn from Knaresborough STW (at 33 km) and from Crimple Beck (at 41.1 km). Ammonium predictions are peaked during the summer at the reach output immediately downstream of Harrogate (N). Downstream of this reach ammonium decreases due to nitrification, and thereafter increases only due to the additional polluted inputs. During the winter only modest increases in ammonium concentrations are evident. Nitrate predictions increase greatly during the summer (less so in the winter), downstream of each of the pollution inputs, eventually decreasing due to dilution from tributaries in the lower reaches of the Nidd. BOD predictions also increase slightly after each major STW and tributary input. DO predictions during the summer are greatly affected by the STW inputs, showing the classic "oxygen sag" behaviour downstream of Harrogate, returning to normal levels approximately 7 km downstream, although observations suggest a less servere effect on DO. Below this the STW inputs from Knareborough and from Crimple Beck cause further depletion of DO. Overall the predictions follow the observations reasonably well.

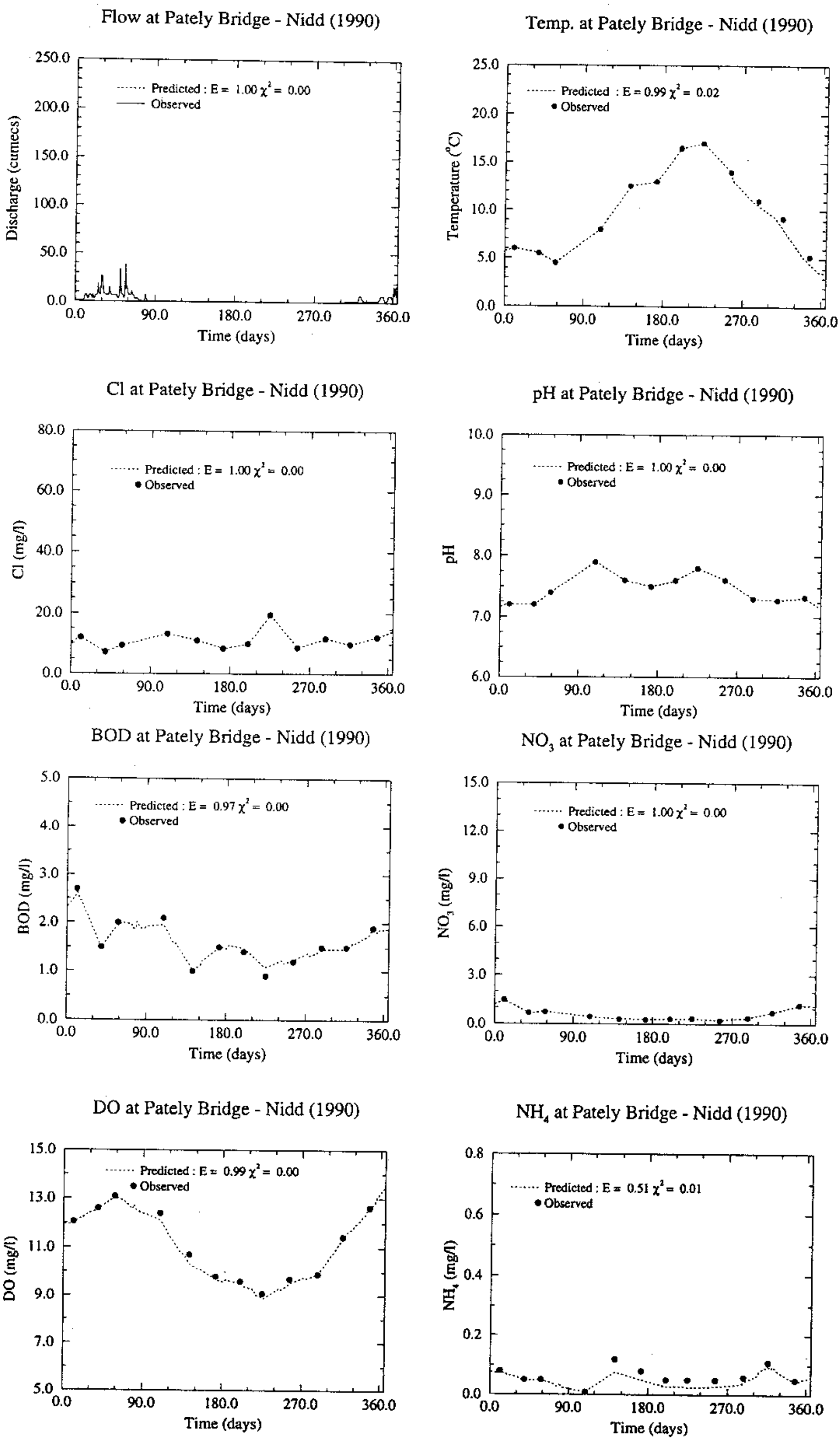


Figure 19 **QUASAR predictions compared with NRA observations, Pately Bridge - Nidd (1990)**

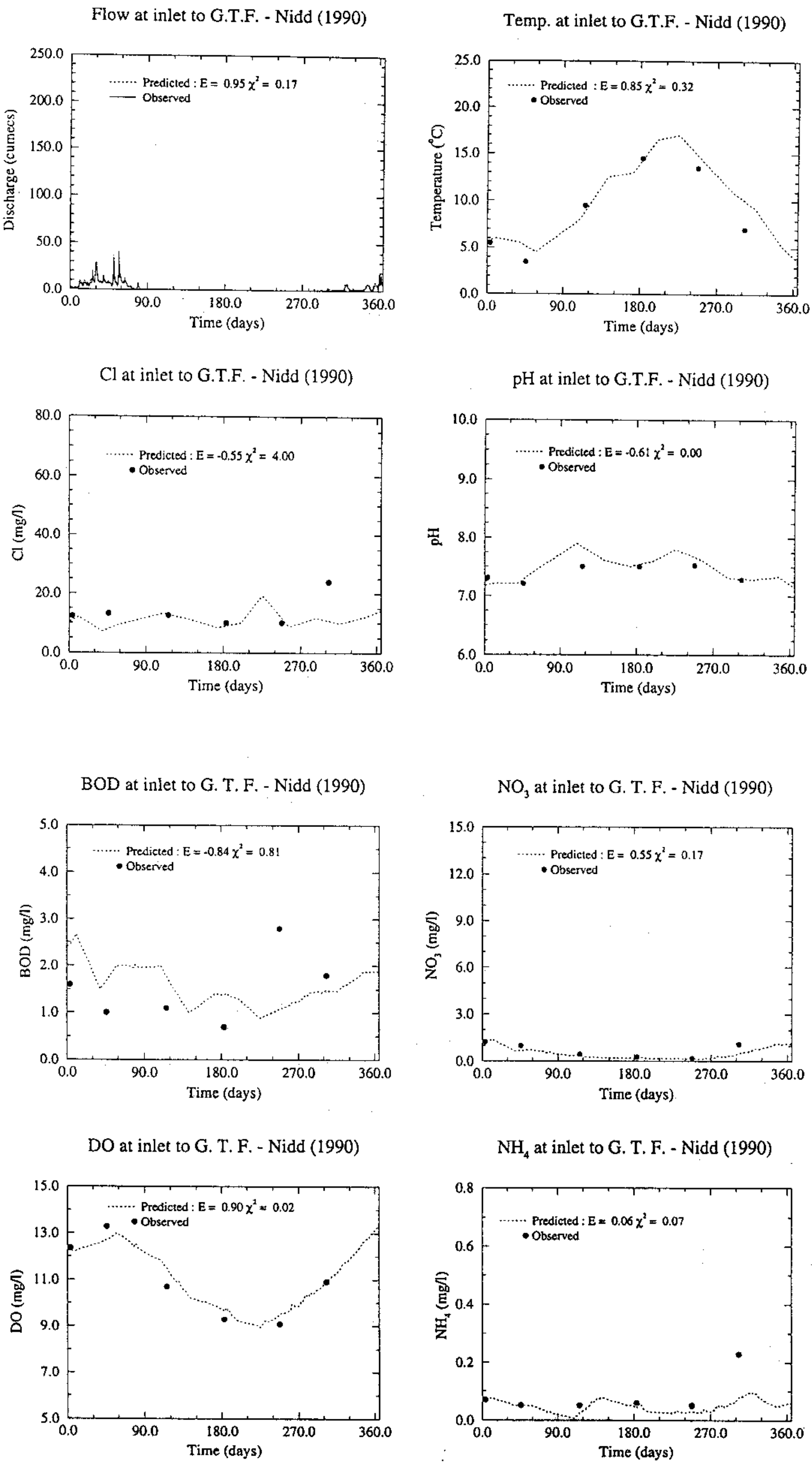


Figure 20 QUASAR predictions compared with NRA observations, inlet to G.T.F. - Nidd (1990)

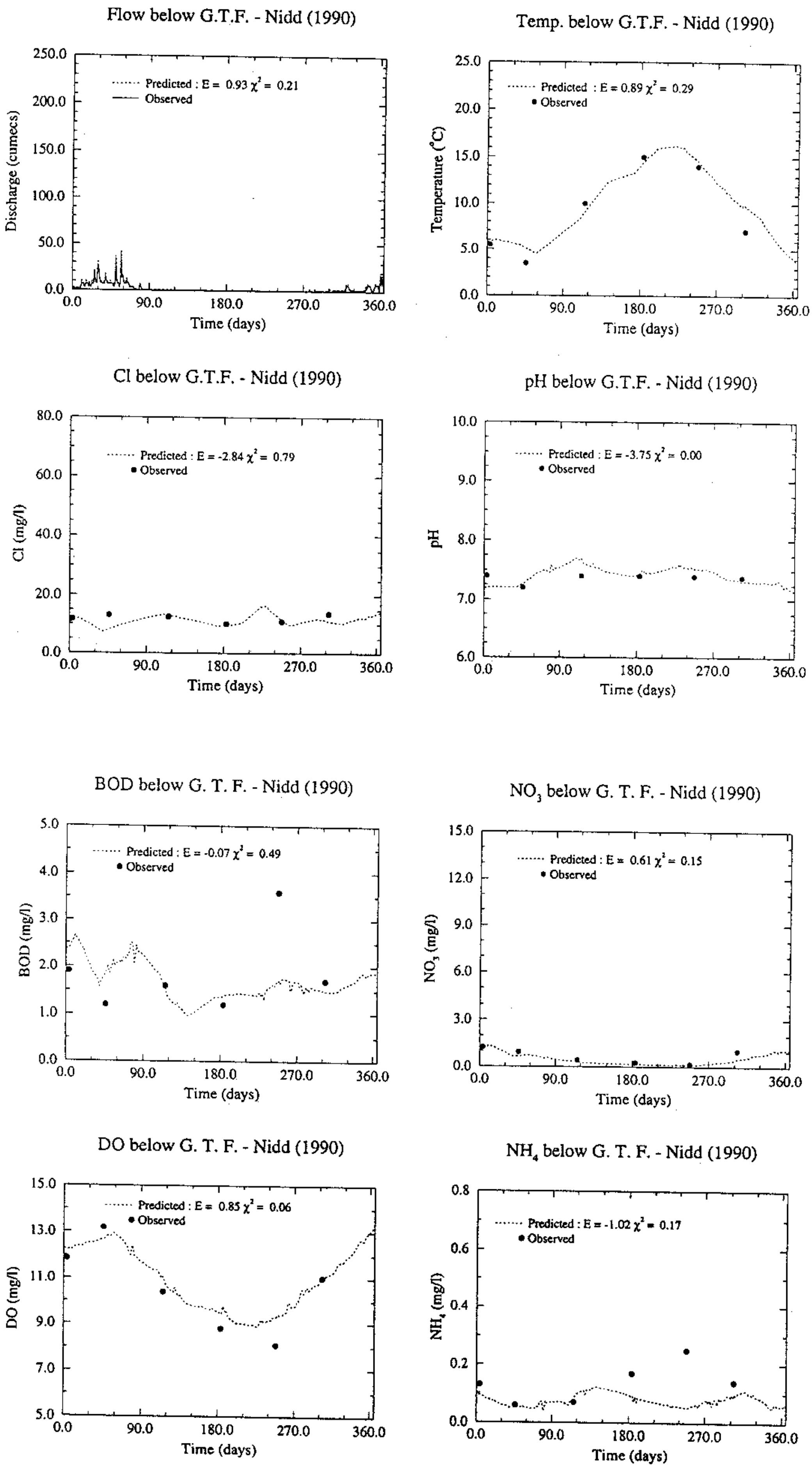


Figure 21 QUASAR predictions compared with NRA observations, below G.T.F. - Nidd (1990)

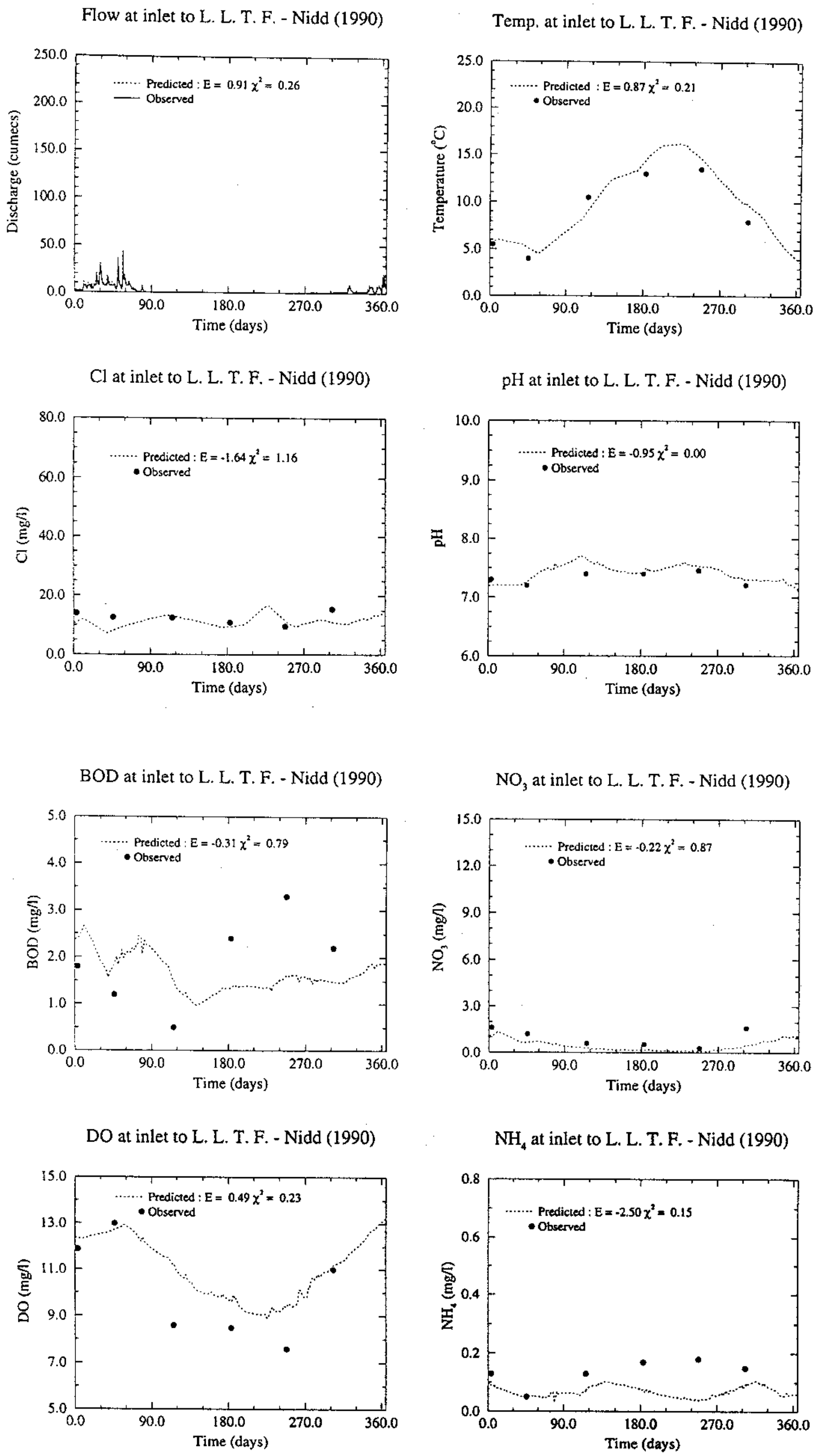


Figure 22 **QUASAR predictions compared with NRA observations, inlet to L.L.T.F. - Nidd (1990)**

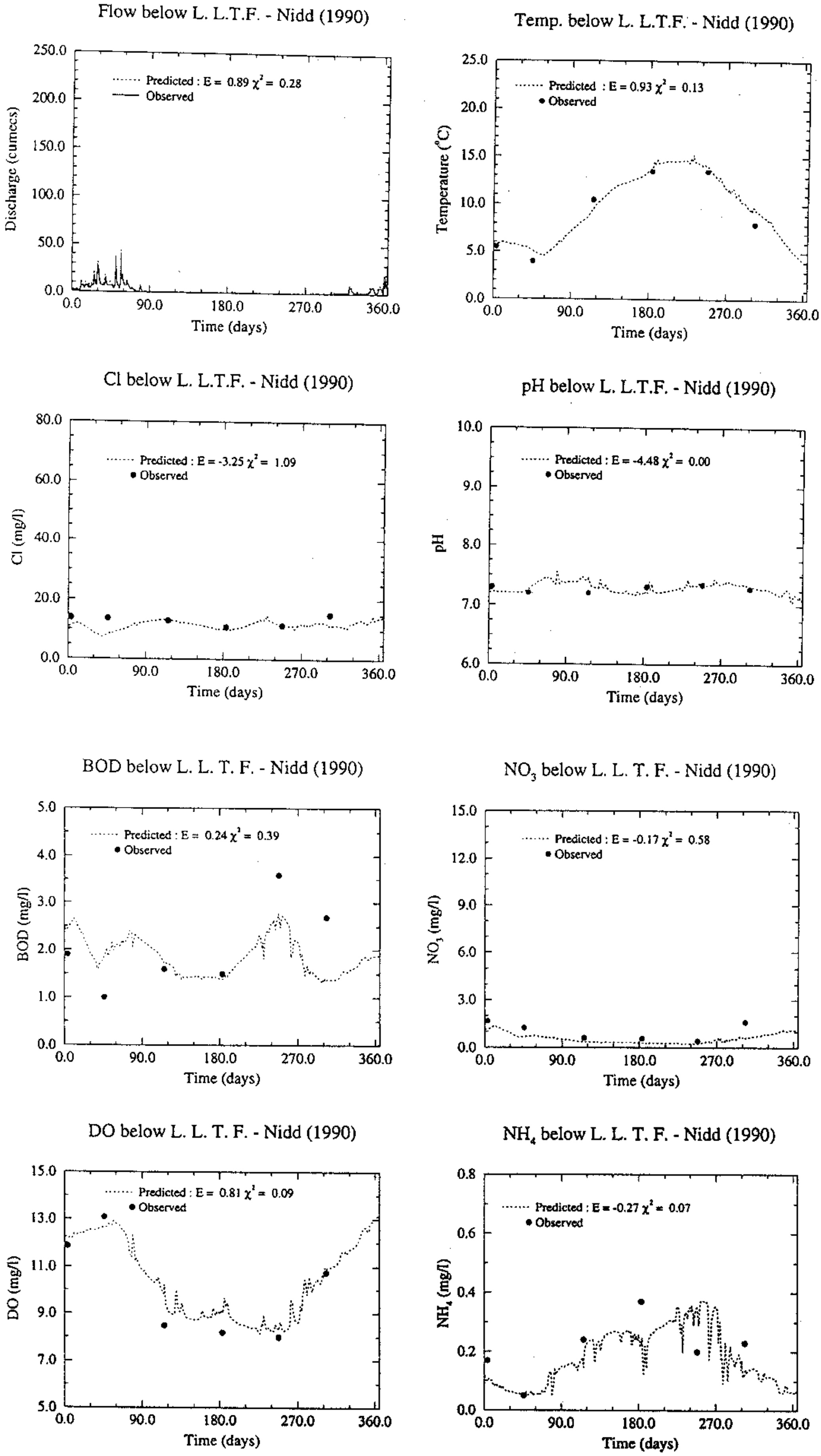


Figure 23 **QUASAR predictions compared with NRA observations, below L.L.T.F. - Nidd (1990)**

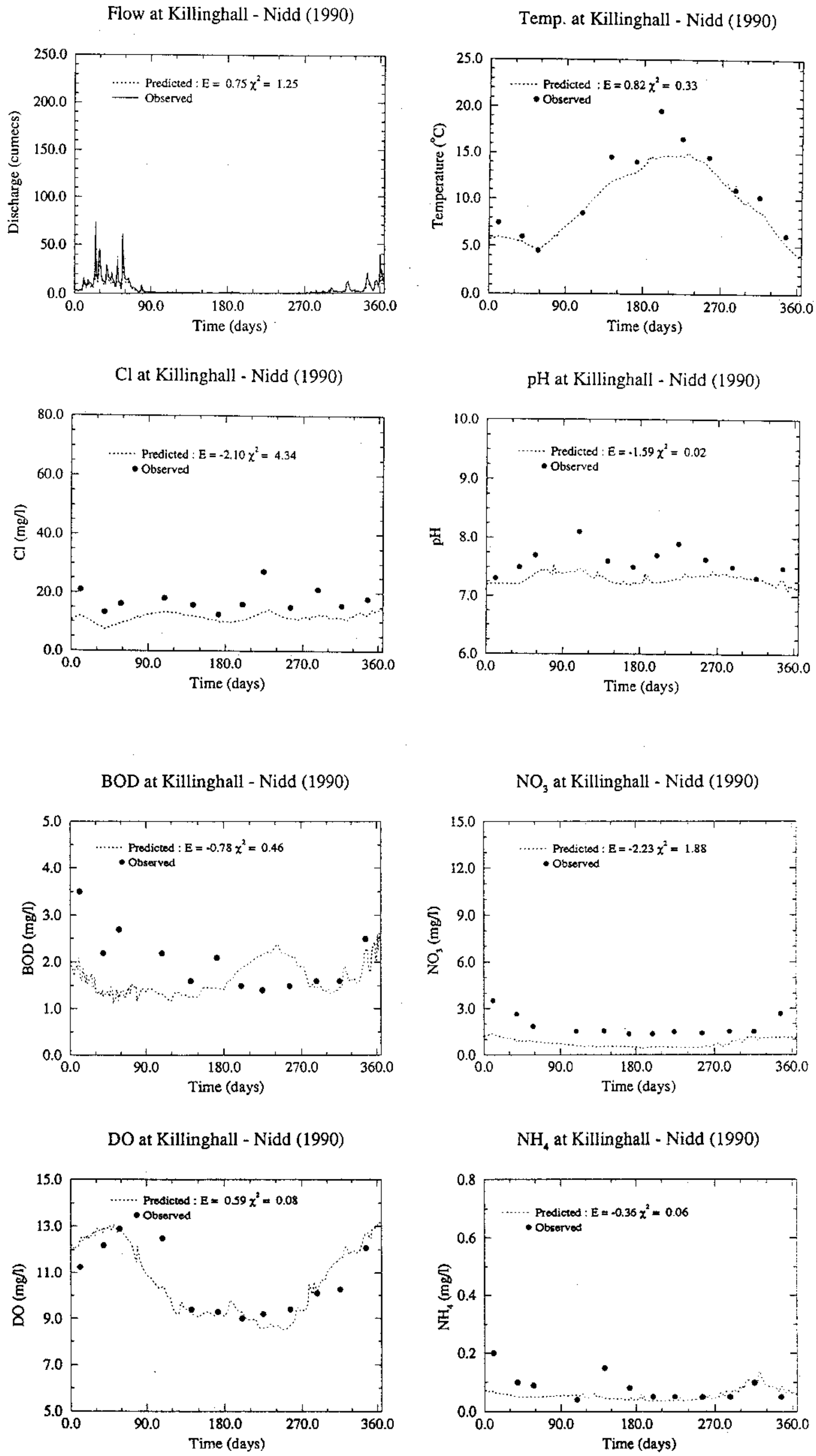


Figure 24 QUASAR predictions compared with NRA observations, Killinghall - Nidd (1990)

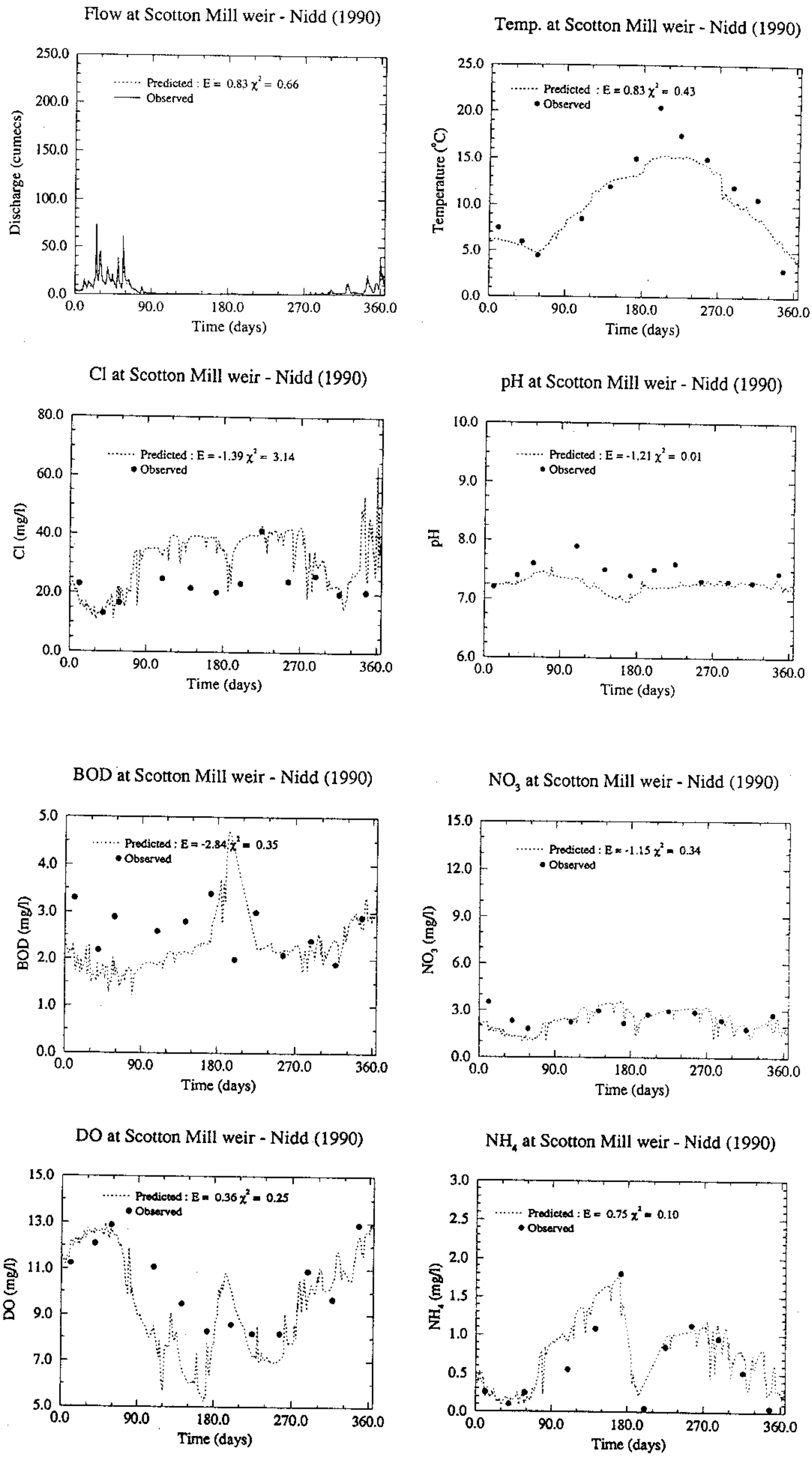


Figure 25 **QUASAR predictions compared with NRA observations, Scotton Mill weir - Nidd (1990)**

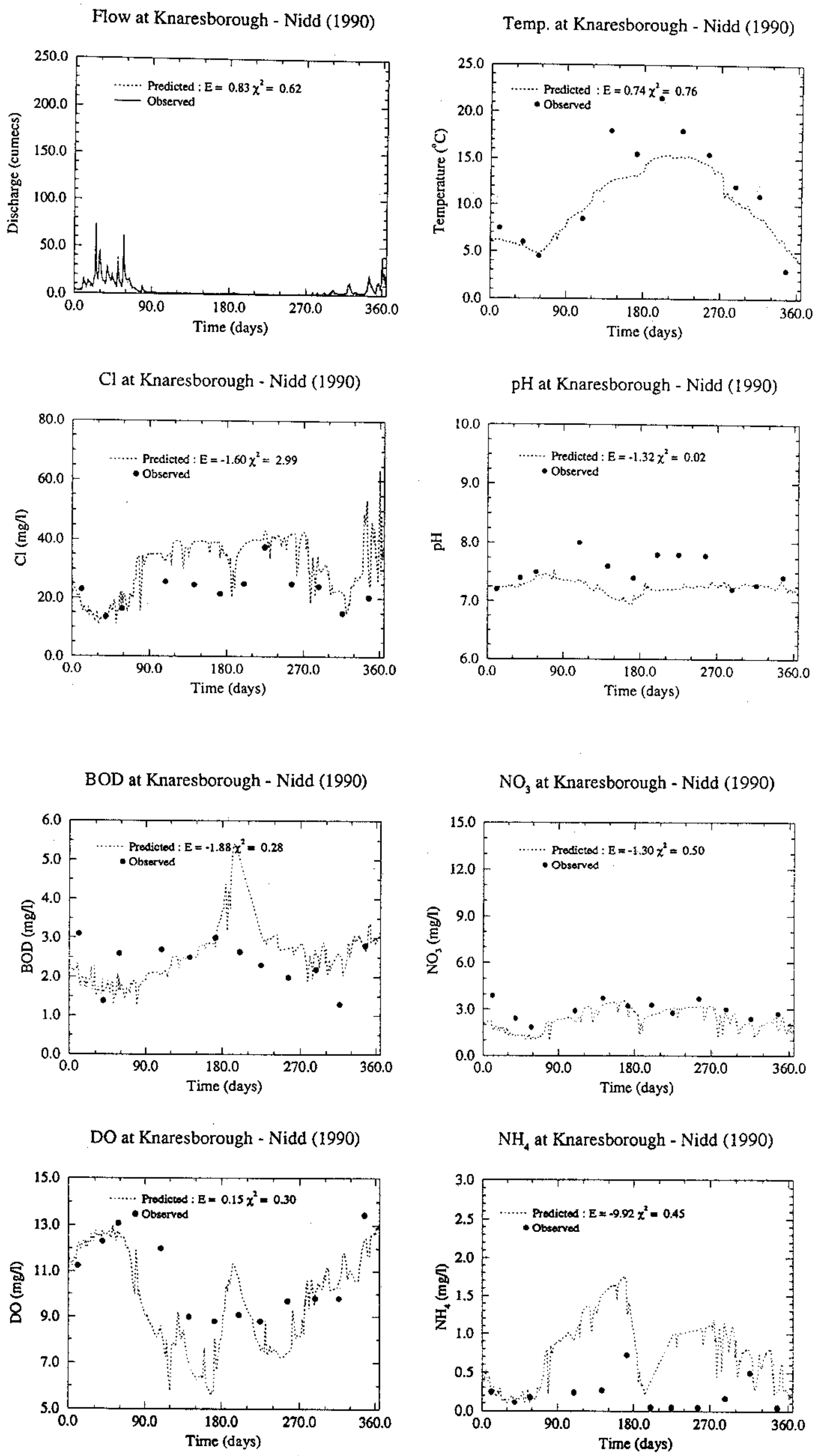


Figure 26 **QUASAR predictions compared with NRA observations, Knaresborough - Nidd (1990)**

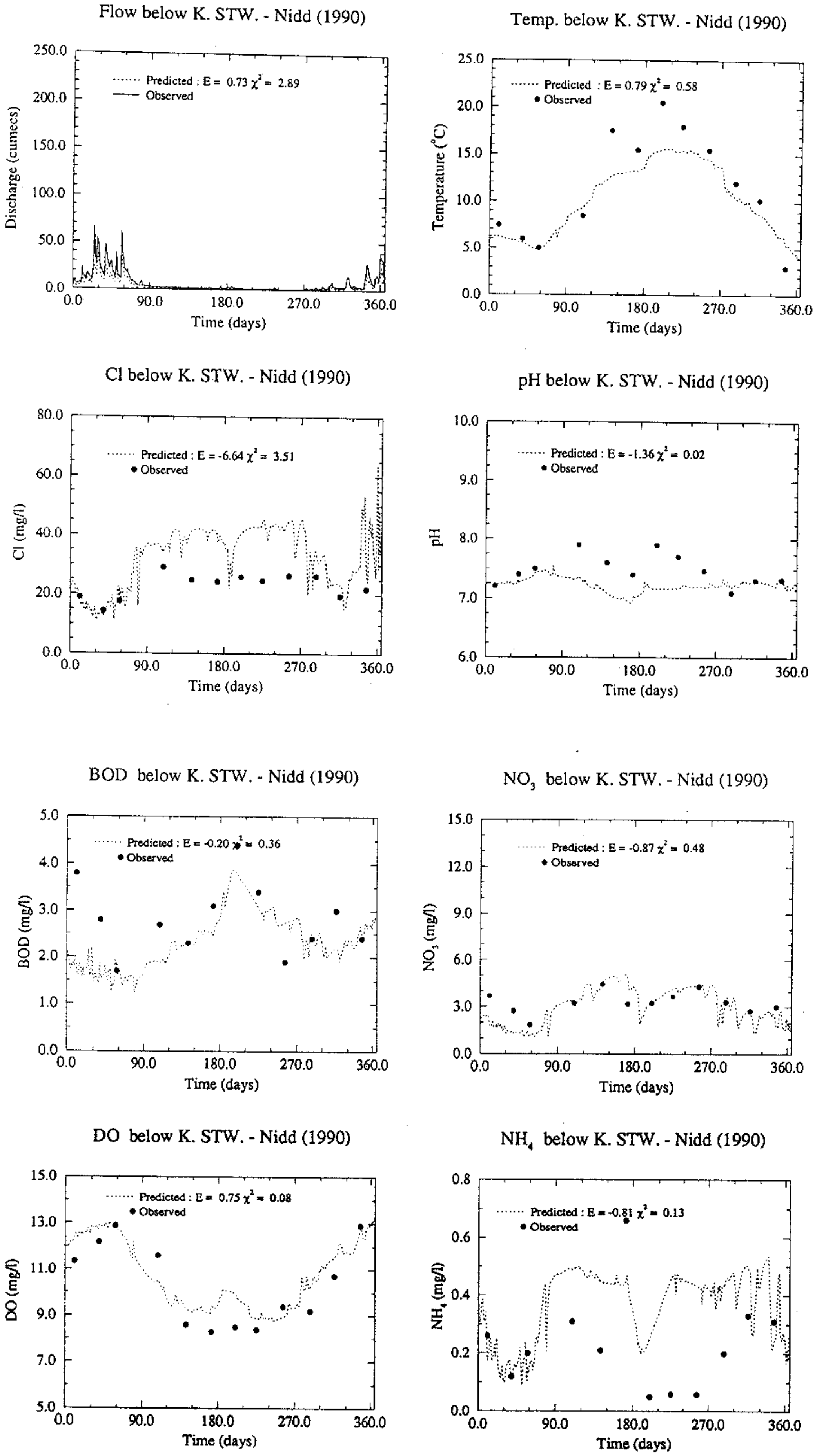


Figure 27 QUASAR predictions compared with NRA observations, below K.STW. - Nidd (1990)

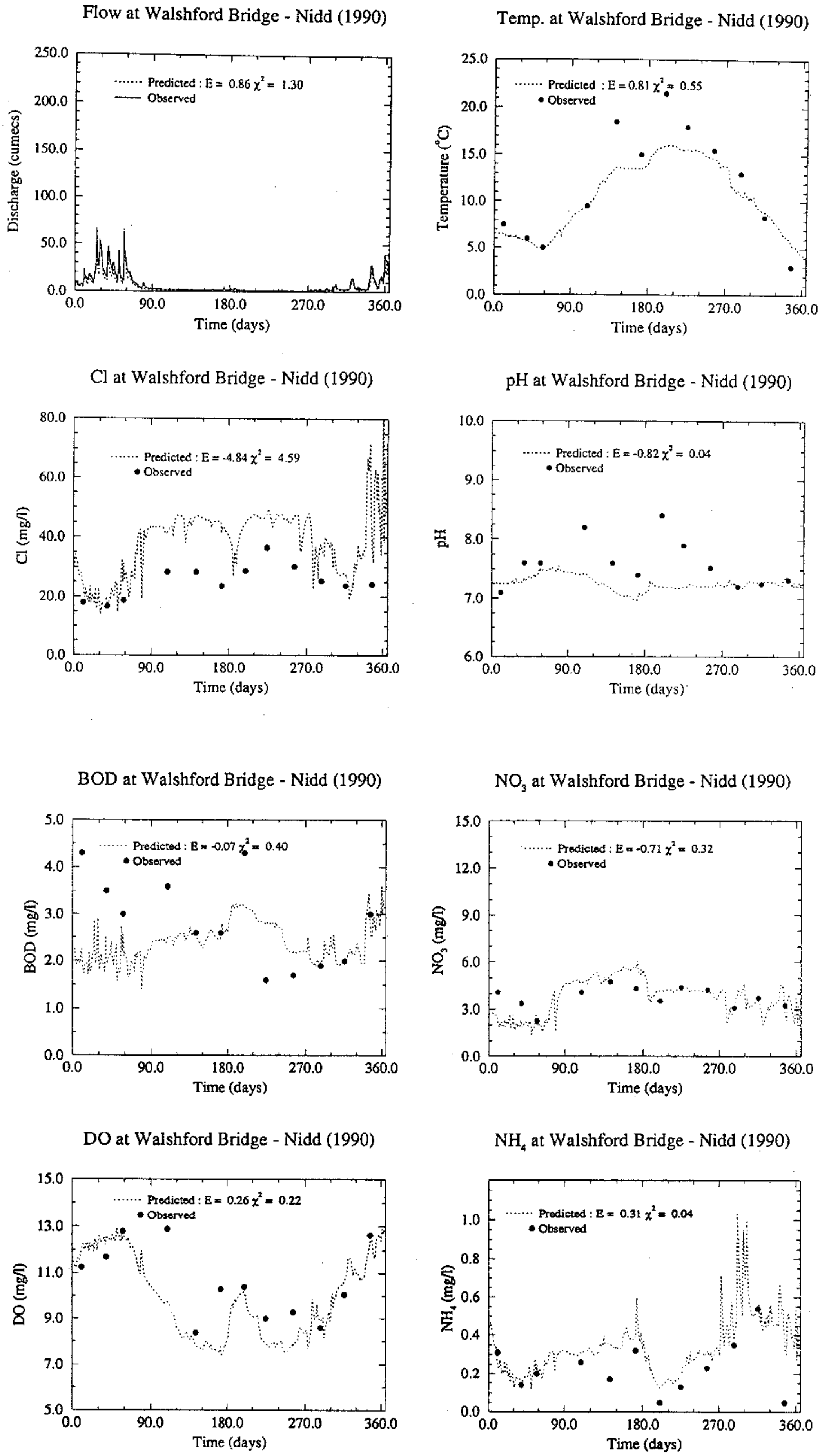


Figure 28 **QUASAR predictions compared with NRA observations, Walshford Bridge - Nidd (1990)**

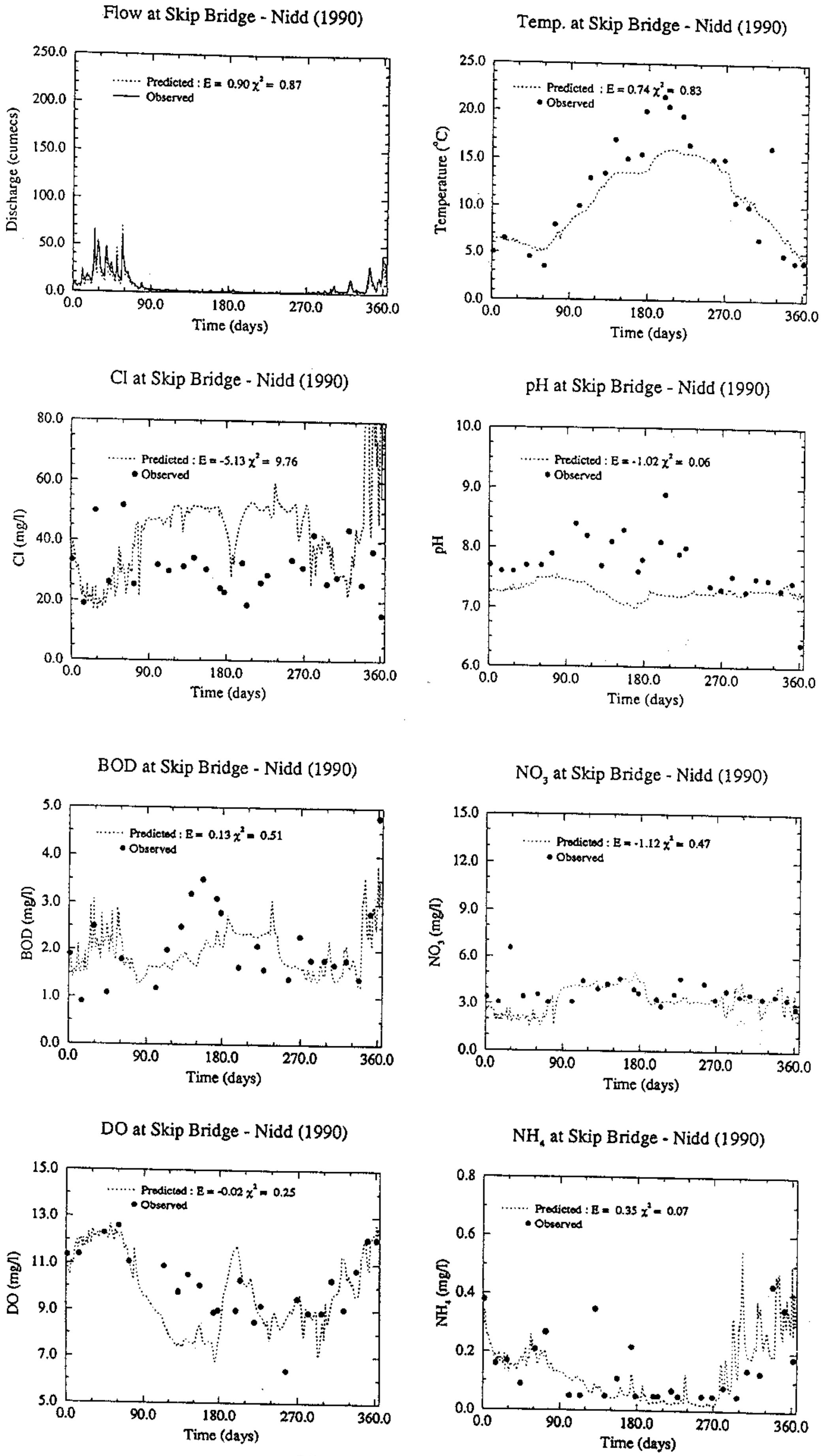


Figure 29 QUASAR predictions compared with NRA observations, Skip Bridge - Nidd (1990)

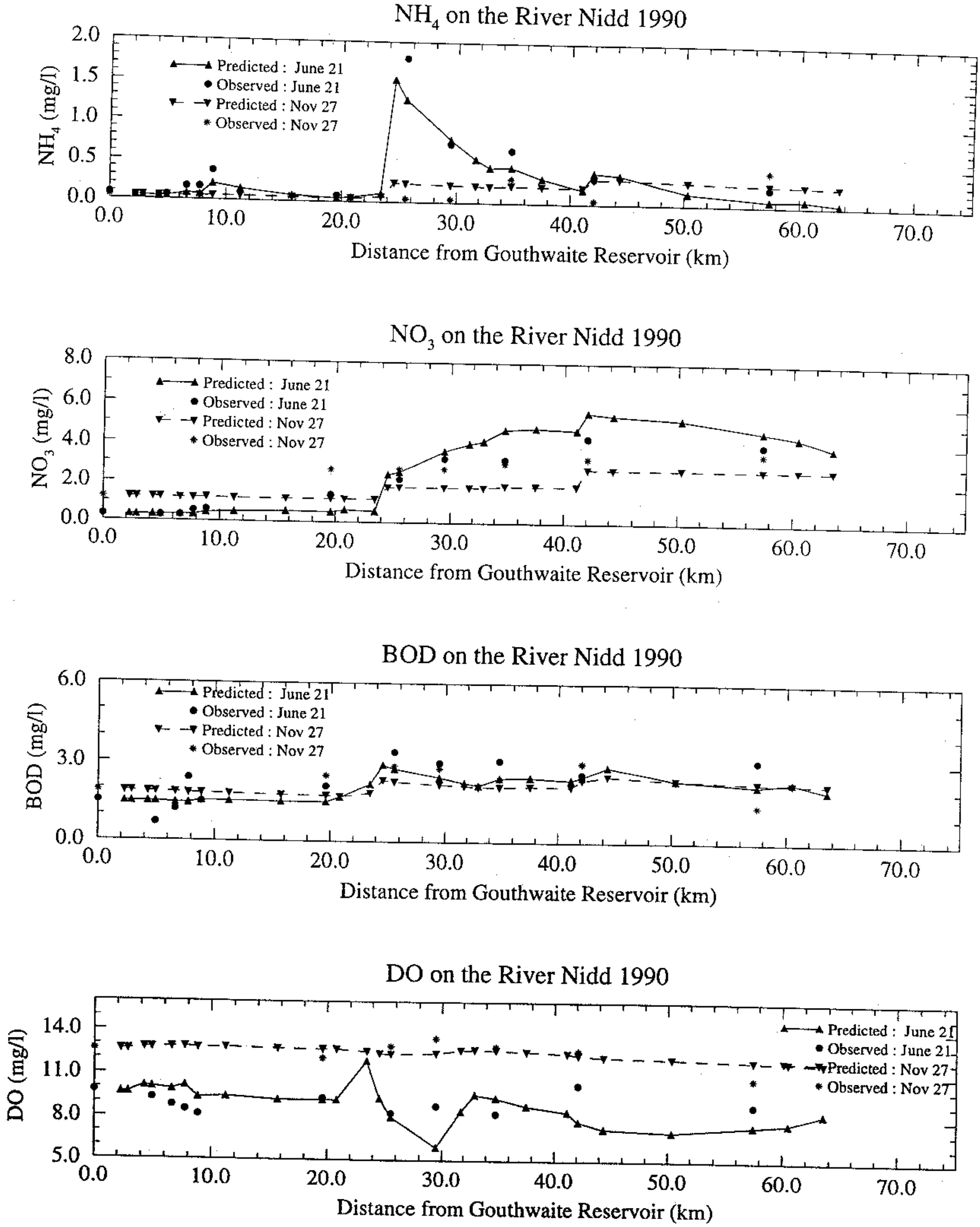


Figure 30 QUASAR predictions compared with NRA observations, along the River Nidd on June 21 and December 13 (1990).

5.4 RIVER OUSE

Figures 31 and 32 show the calibration results at the WQ sites at Aldwarke Bridge and Skelton, just north of York, on the River Ouse. In this case the stretches of river from the confluence of the Ure and the Swale down to Aldwarke Bridge and the stretch from Aldwarke Bridge to Skelton were both calibrated.

The predictions of the conservative determinands at the two WQ sites agree well with the observations, with efficiency factors exceeding 40% for the chloride and pH predictions, and efficiency factors exceeding 85% for temperature and a value of 69% for the flow at Skelton. Observed flow in the Alwarke Bridge figure is actually that observed at Skelton, so again a flow comparison is only approximate here.

Non-conservative determinand predictions at Aldwarke Bridge and Skelton agree well with the observations. Nitrate and DO concentrations give particularly good comparisons with efficiency factors greater than 40% and 55% respectively. Ammonium is better predicted at Aldwarke Bridge than at Skelton which has a greater variability in the observations possibly due to non-point source inputs in this intensively cultivated arable area. The BOD observations follow the pattern of the River Ure (due to the larger flows of the Ure compared to the Nidd and Swale) with an increase in BOD during the months June to August probably due to algal growth. This peak would be better predicted if algal concentrations were explicitly modelled in the Ouse catchment.

Figure 33 shows the non-conservative determinand predictions for each reach and the NRA observations taken at certain points along the Ouse on June 22 and November 26, 1990 (the predicted flow from the first reach downstream of the Swale confluence was 13.9 and 35.3 cumecs respectively). The predicted concentrations out of each reach are remarkably consistent along this part of the river due to the large flows of the Ouse. Polluted waters from the River Kyle (at 6.3 km from the Swale confluence) and from the River Nidd (at 8.5 km) areeasily assimilated by the Ure. Generally predictions follow the observations reasonably well.

5.5 CONCLUSION

Overall the predictions of the QUASAR conservative determinands, and the determinands describing the basic BOD-DO relationships compare reasonably well with the NRA observations throughout the Ouse system above York. A number of discrepancies have been identified in this Section which require further investigation, and which coupled with detailed observations will lead to improved process descriptions in the model. However this calibration work and the parameters determined for each of the river systems can now be used to verify or estimate the appropriateness of the present model description. Section 6 describes the results of a basic sensitivity analysis of QUASAR while Section 7 will describe the validation work carried out as the next stage in testing the model.

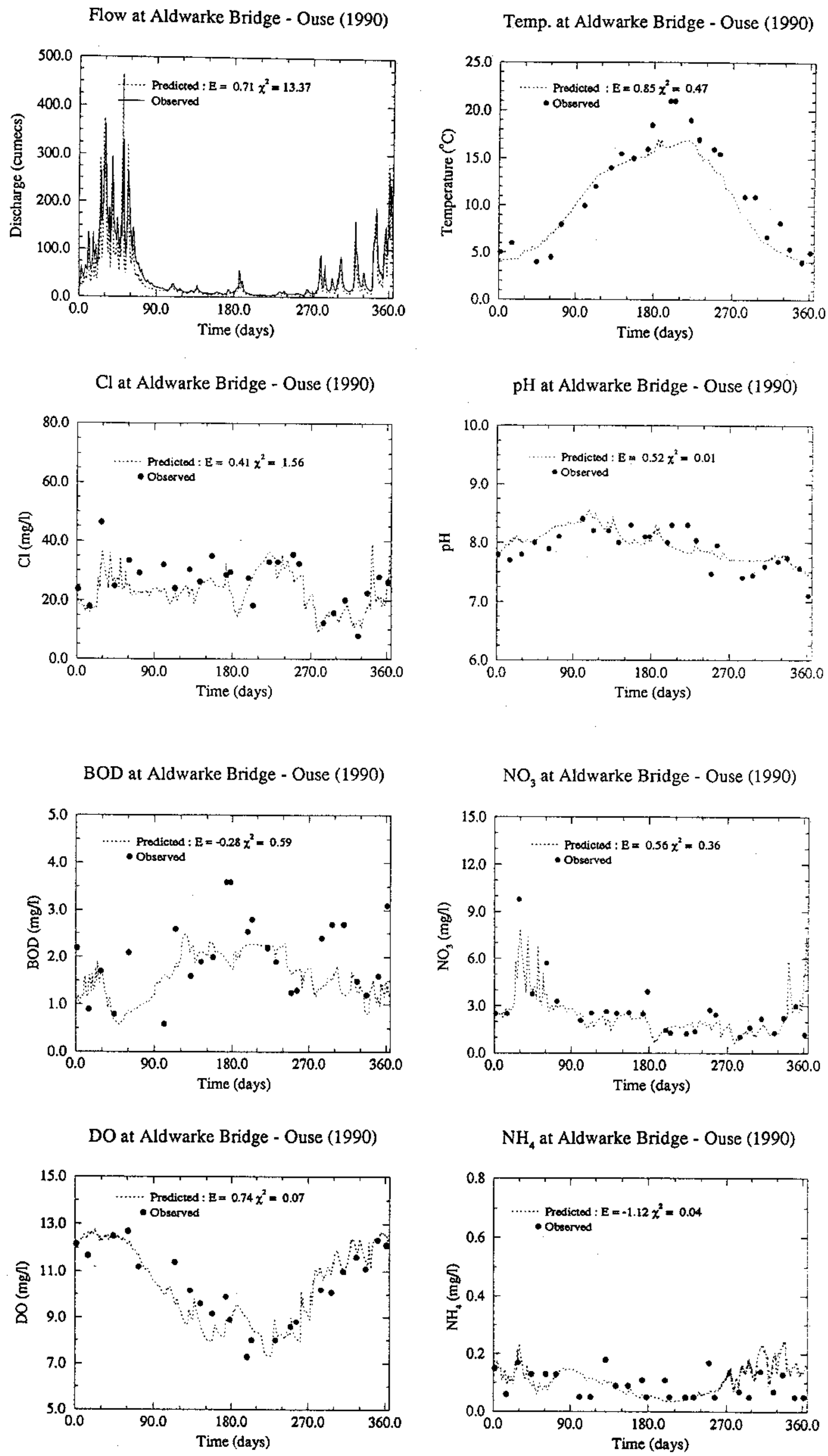


Figure 31 QUASAR predictions compared with NRA observations, Aldwarke Bridge - Ouse (1990)

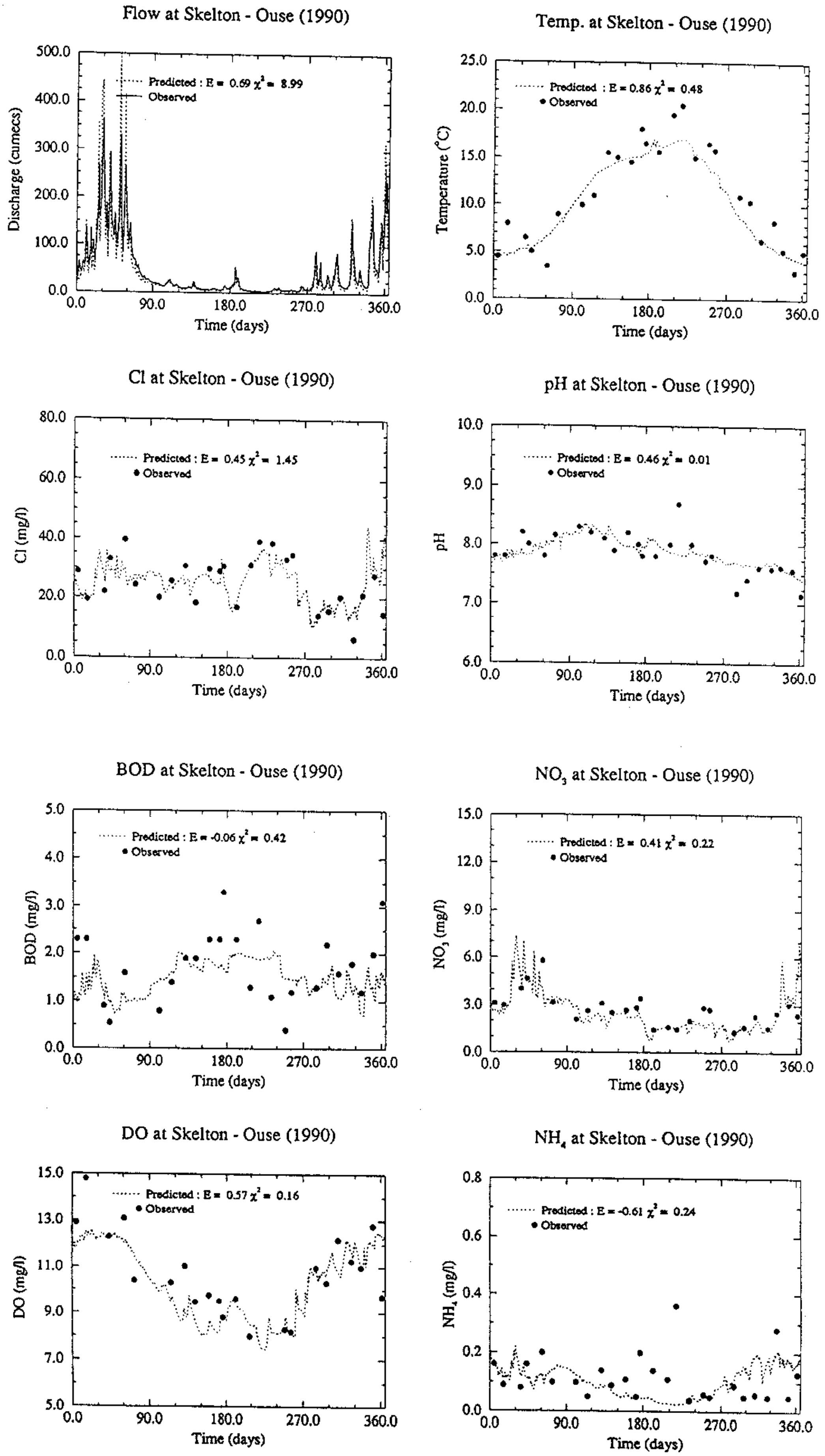


Figure 32 QUASAR predictions compared with NRA observations, Skelton - Ouse (1990)

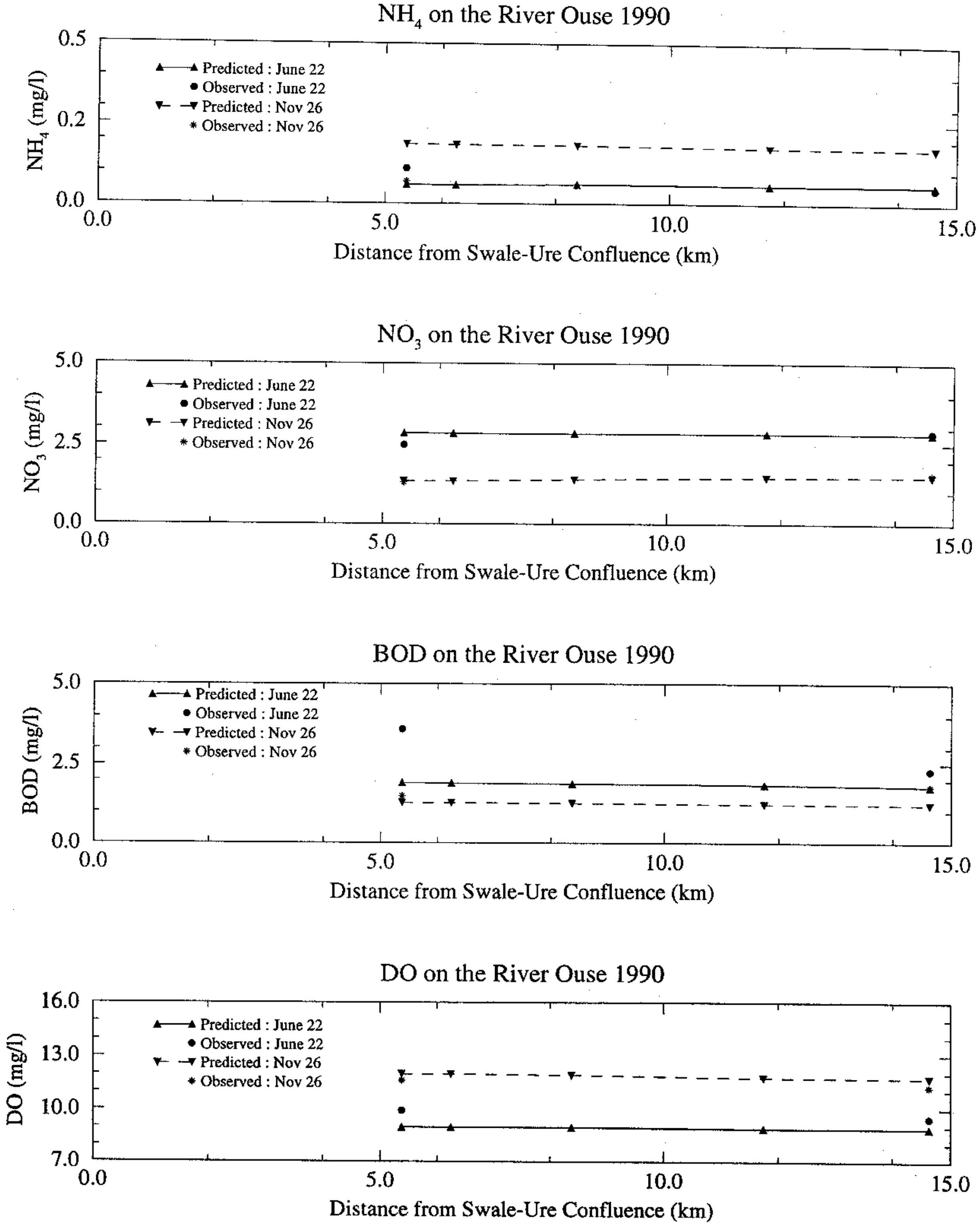


Figure 33 QUASAR predictions compared with NRA observations, along the River Ouse on June 22 and November 22 (1990).

6 Sensitivity Analysis

6.1 METHODOLOGY

In order to carry out a basic sensitivity analysis of QUASAR, the River Swale reach structure and network was chosen to represent a typical river network. Furthermore, in order to simplify the representation of the river and to reduce the number of parameters in the analysis, each reach was assigned the same rate coefficients for each simulation run. This simplified set of rate parameters is refered to here as the base line simulation set and the values used are shown in Table 17.

The method used in this analysis was to vary the simplified set of parameters individually and to see the corresponding effects on the chemistry of each of the non-conservative determinands. To this end the value of each base line rate coefficient is increased and decreased by a factor of 2 as this was thought a reasonably wide variation in the parameter values. The changes to all the non-conservative determinands brought about by this variation of the parameters is shown in individual figures and described in Section 6.2. A more rigorous sensitivity analysis in which sensitivity coefficients (Beck, 1983) are calculated can be carried out, but the effort is complicated by the model time series inputs which are markedly variable.

Table 17 *Rate coefficients used in the sensitivity analysis simulations on the River Swale*

Rate coefficient	*Base line set*	*Lower limit set*	*Upper limit set*
Denitrification	*0.08*	*0.04*	*0.16*
BOD decay	*0.09*	*0.045*	*0.18*
Nitrification	*0.10*	*0.05*	*0.20*
O_2 - Sediment	*0.08*	*0.04*	*0.16*
BOD - Algae	*0.10*	*0.05*	*0.20*
Photo. O_2 <50µg/l	*0.04*	*0.02*	*0.08*
Photo. O_2 >50µg/l	*0.01*	*0.01*	*0.01*
BOD - Sed.	*0.08*	*0.04*	*0.16*
Algae Resp.	*0.14*	*0.14*	*0.14*
Algae Resp. Slope	*0.013*	*0.0065*	*0.026*

6.2 SIMULATION RUNS

6.2.1 Nitrification rate

Figure 34 shows the effect of changing the nitrification rate between the two limits. The greatest effect of these changes is shown during the summer months, when the ammonium concentrations vary by up to ±80%, although there is also a reduced effect during the wet months. This is to be expected since during the dry months flows are low and reach residence times are high, allowing chemistry a significant time to take place in each reach. The nitrification rate has a minimal effect on the nitrate concentrations and only slightly more so on the DO for the Swale simulation. It should be noted that the effects on these concentrations also depends upon the value of the ammonium concentration (cf. River Nidd calibration runs where much greater effects were evident). No effect is expected on the BOD concentrations.

6.2.2 Denitrification rate

The effect of changing the denitrification rate between the two limits is shown in Figure 35. Only a small effect is evident with variation of the order of ±10% during the summer months. There is not expected to be any effect on the other determinands.

6.2.3 BOD decay rate

Figure 36 shows the influence of the BOD decay rate on the BOD concentrations. Only a small change in BOD is evident of ±8% for the parameter variations, although a low BOD decay rate was initially chosen as the base line value. These variations produce a modest change in the DO concentrations of ±1 mg/l (or ±15%) during the summer months, with a decrease in DO when the BOD decay rate is increased. No effect is expected on the ammonium and nitrate concentrations.

6.2.4 BOD Sedimentation

The effect of the BOD sedimentation rate coefficient is shown in Figure 37. It is evident that a large change of ±50% in the BOD concentration takes place generally throughout the year, as would be expected from the simple proportionality to the BOD concentration (Appendix 1). A modest change of ±1 mg/l is shown in the corresponding DO concentrations, with a decrease in DO when the sedimentation rate is increased. No effect is expected on the ammonium and nitrate concentrations.

6.2.5 BOD Contribution from Algae

Figure 38 shows the effect of varying the BOD contribution represented by the algal rate coefficient. A large change in the BOD concentrations of ±60% is evident during July/August when the chlorophyll-a concentration is at its peak. A corresponding change of ±1 mg/l results during this period, with a decrease in DO when the algae rate coefficient increases. No effect is expected on the ammonium and nitrate concentrations.

6.2.6 Benthic Oxygen Demand

Variation of the benthic oxygen demand is shown in Figure 39. It is evident that this rate coefficient only effects the DO river concentrations, and by a modest amount (±1 mg/l) which is greatest during the dry months.

6.2.7 Photosynthetic Oxygen production

Figure 40 shows the variation of the DO concentrations when the photosynthetic oxygen production coefficient rate coefficient is changed. This rate coefficient has a significant effect on the DO with a ± 2 mg/l change brought about during the summer when the assumed chlorophyl-a distribution is peaked, with DO decreasing as the coefficient decreases. No other determinand is affected.

6.2.8 Respiration

The effect of varying the respiration rate coefficient is shown in Figure 41. This rate coefficient only has a modest effect (± 1 mg/l) on the DO concentrations during the summer months. No other determinand is affected.

6.2.9 Photosynthesis and Respiration

Figure 42 shows the combined effect of varying the photosynthesis and respiration processes, as they both involve the algae concentrations. As would be expected, the combination leads to smaller overall effects (± 1.5 mg/l) than with photosynthesis alone as respiration essentially has the opposite effect.

6.2.10 Flow parameter

In order to consider the effect on the chemistry of changes in flow conditions, the b parameter in the QUASAR velocity-discharge relationship was varied. As shown in Figure 43, there are significant changes produced for all of the non-conservative determinands. Increasing this parameter results in a smaller reach time constant which reduces the time available for transformations to take place. For example, this has the effect of increasing ammonium concentrations during the summer for the upper value of b with a corresponding decrease in the amount of DO used, thereby leading to an increase in DO. Similarly nitrate and BOD concentrations increase as the time constant decreases.

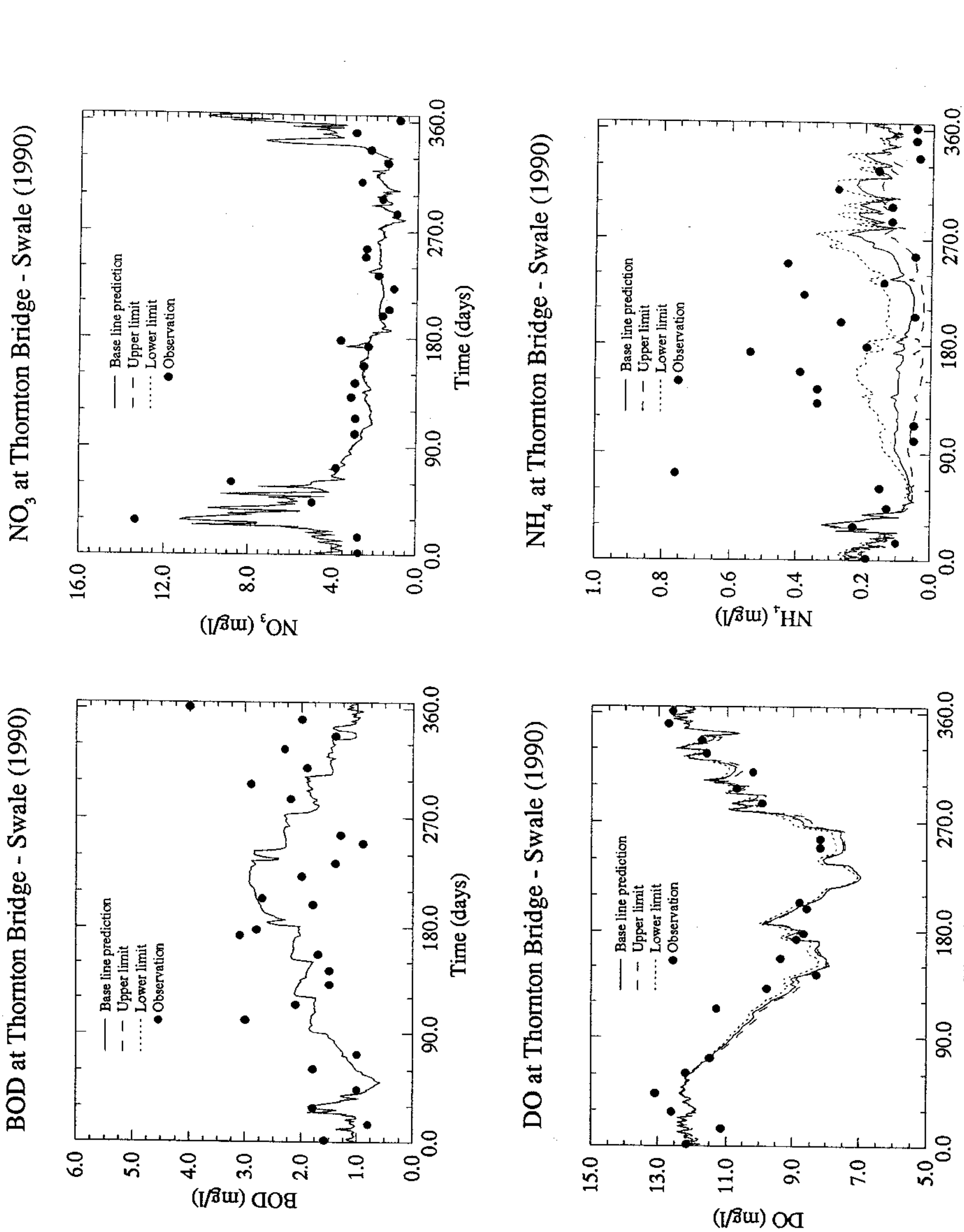


Figure 34 **Sensitivity analysis carried out on the River Swale data set: variation of the nitrification rate coefficient**

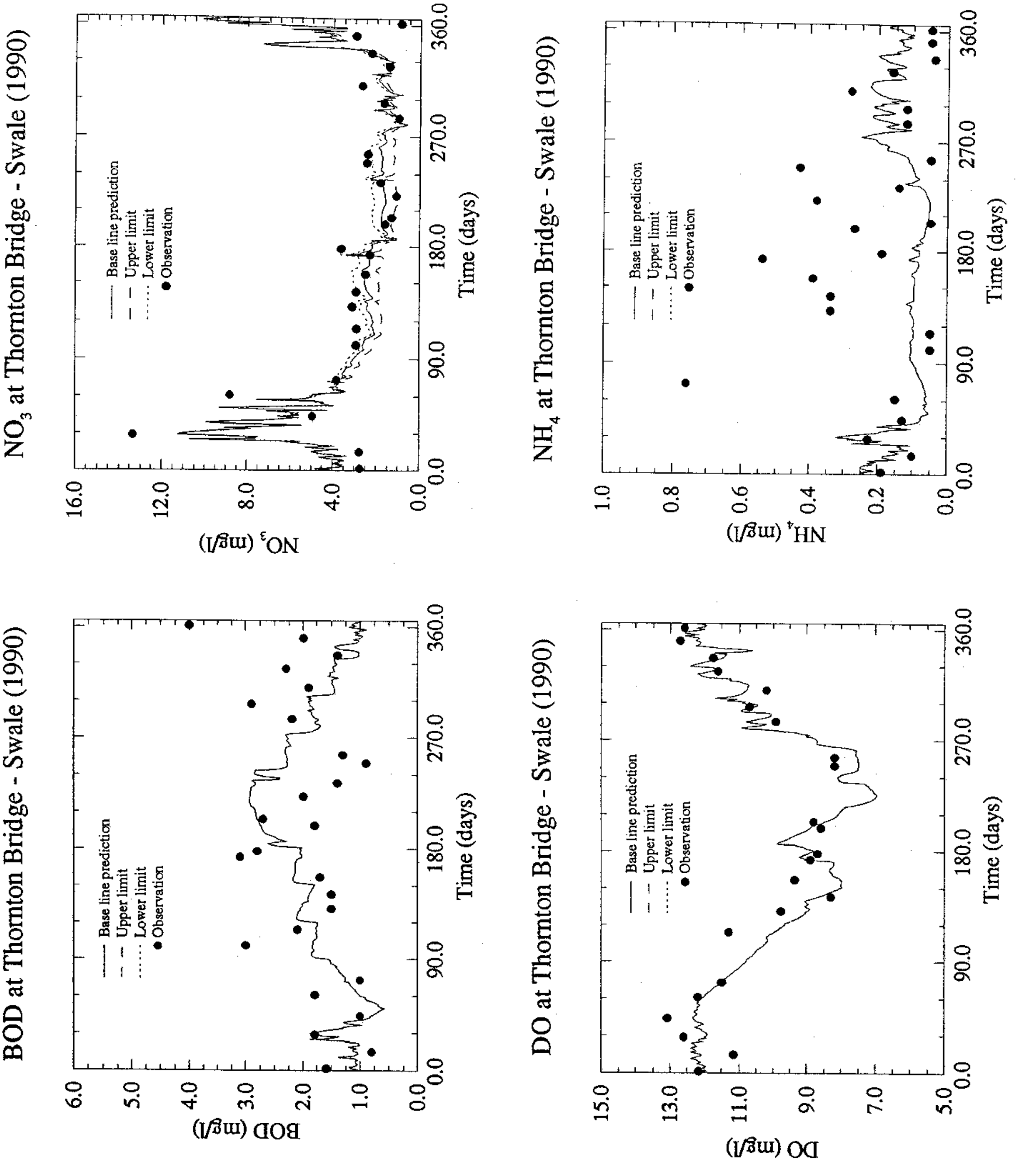


Figure 35 Sensitivity analysis carried out on the River Swale data set: variation of the denitrification rate coefficient

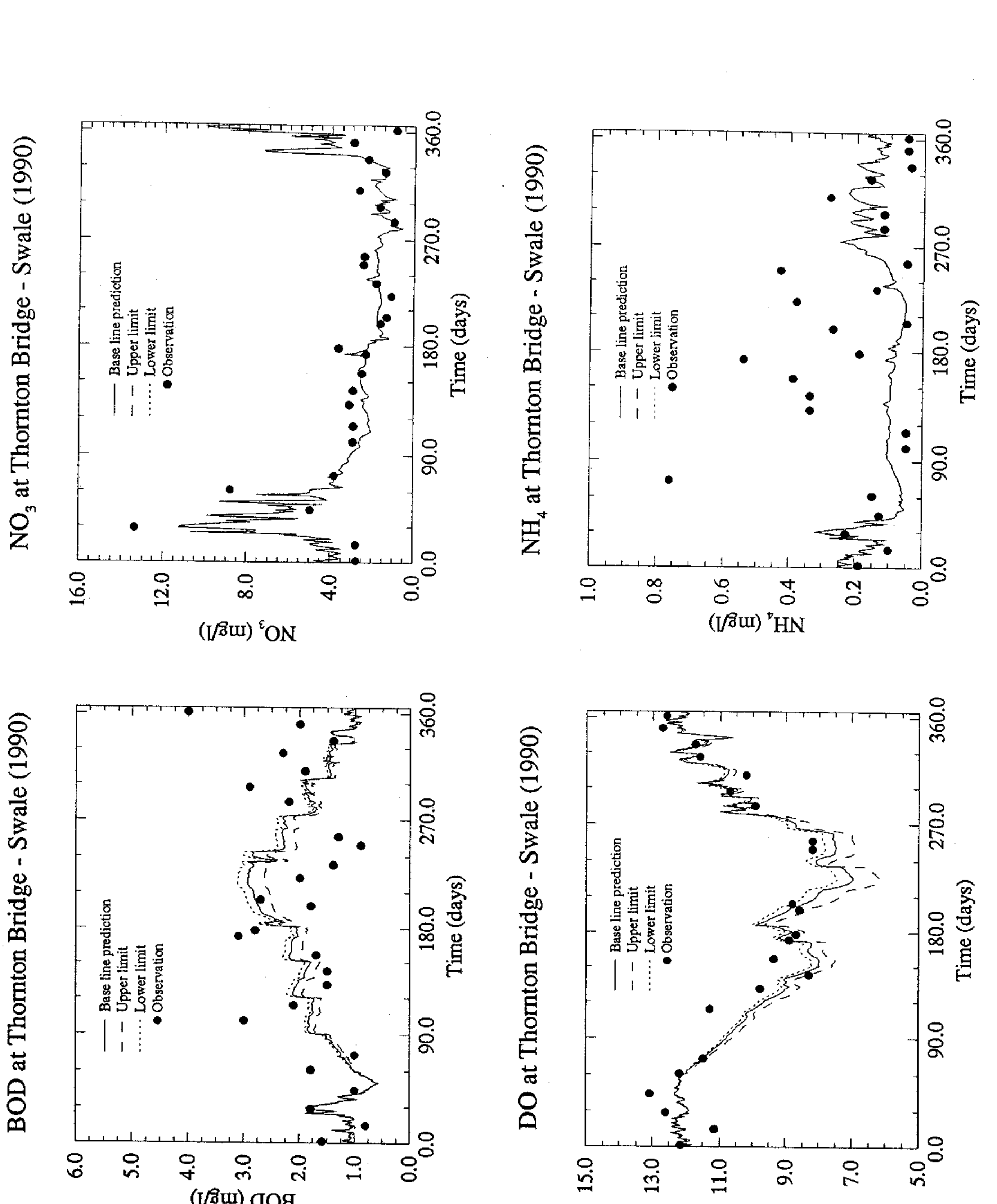


Figure 36 Sensitivity analysis carried out on the River Swale data set: variation of the BOD decay rate coefficient

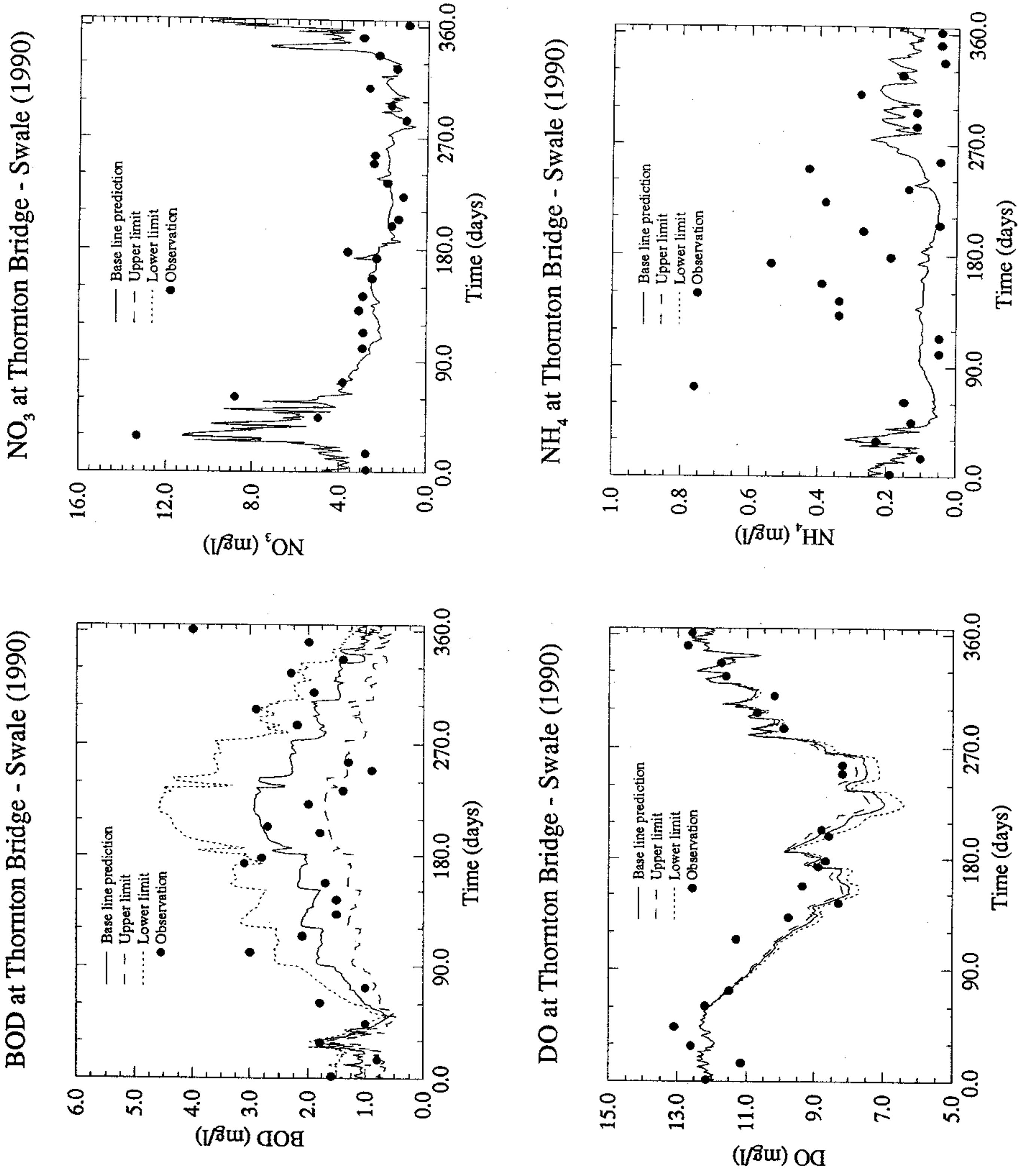


Figure 37 Sensitivity analysis carried out on the River Swale data set: variation of the BOD sedimentation rate coefficient

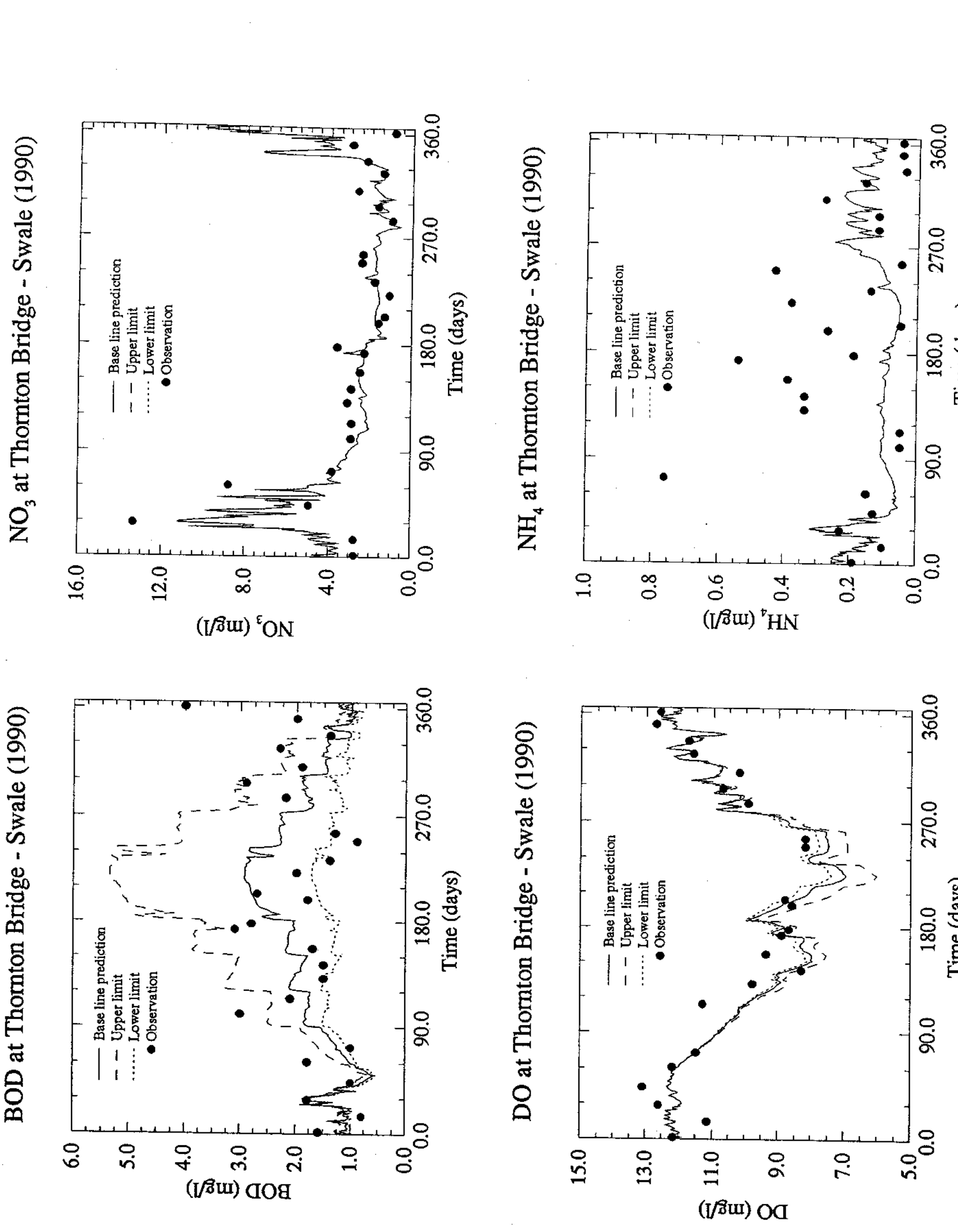


Figure 38 **Sensitivity analysis carried out on the River Swale data set: variation of the BOD contribution from algae rate coefficient**

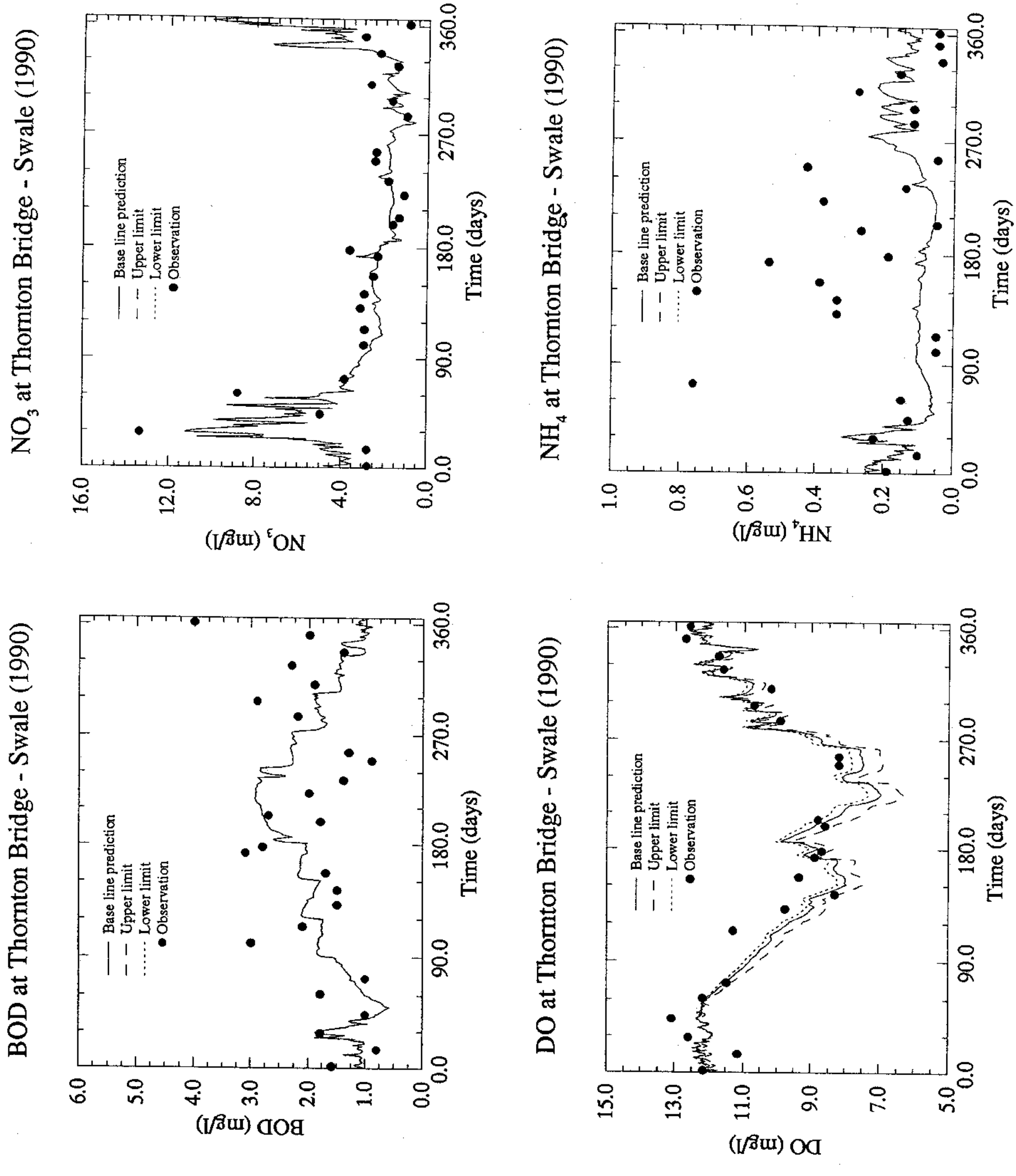


Figure 39 **Sensitivity analysis carried out on the River Swale data set: variation of the Benthic oxygen demand rate coefficient**

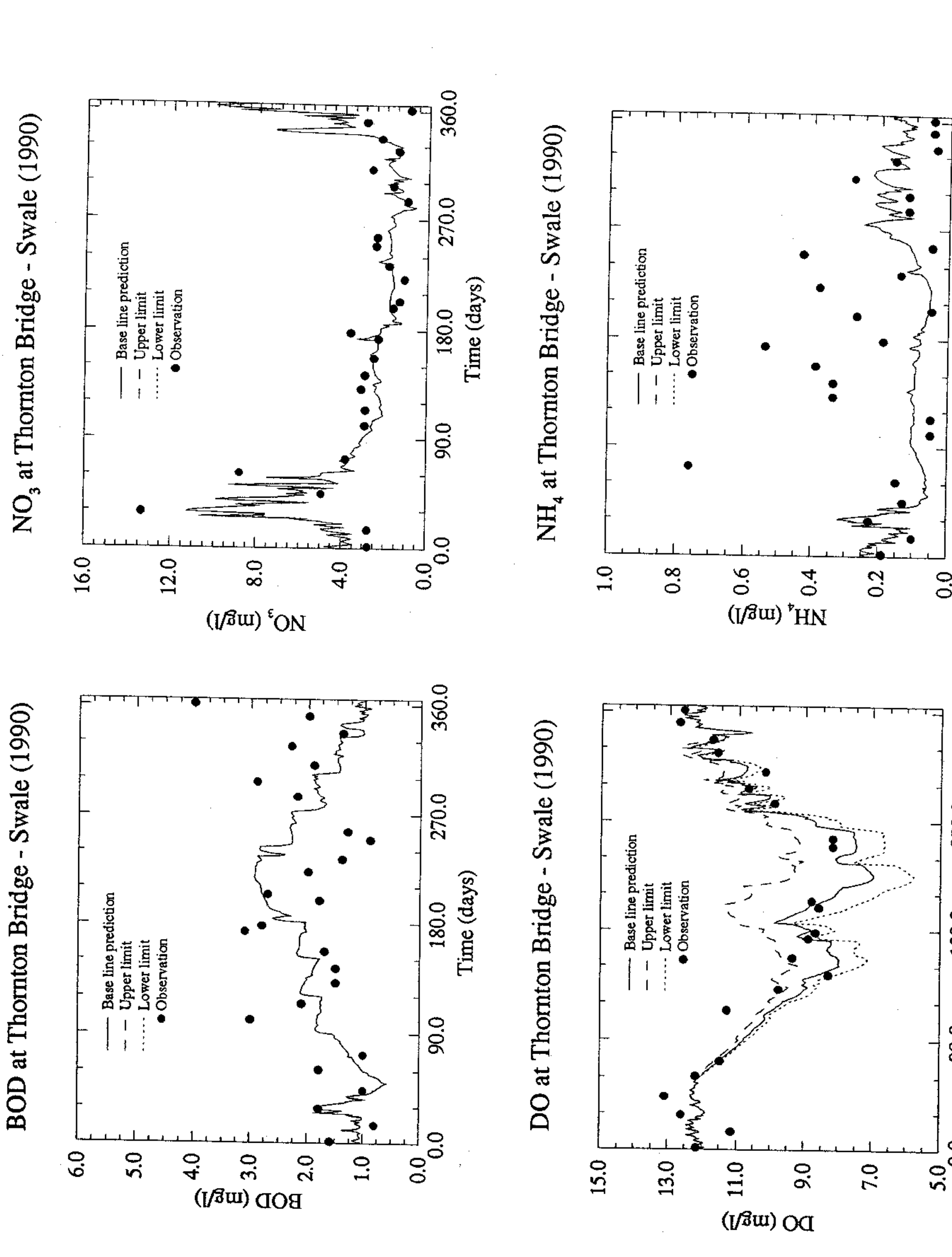


Figure 40 **Sensitivity analysis carried out on the River Swale data set: variation of the photosynthetic oxygen production rate coefficient**

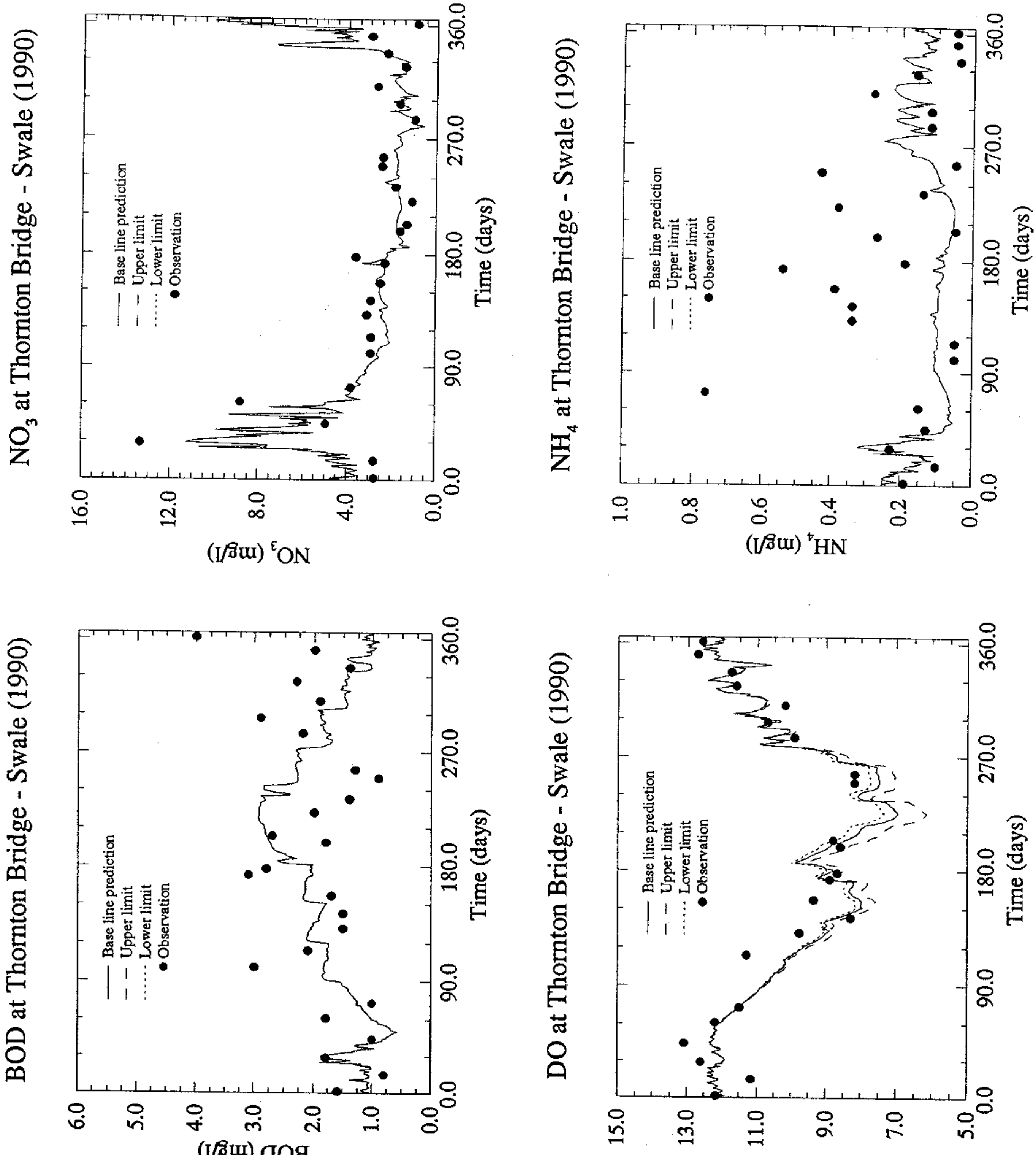


Figure 41 Sensitivity analysis carried out on the River Swale data set: variation of the respiration rate coefficient

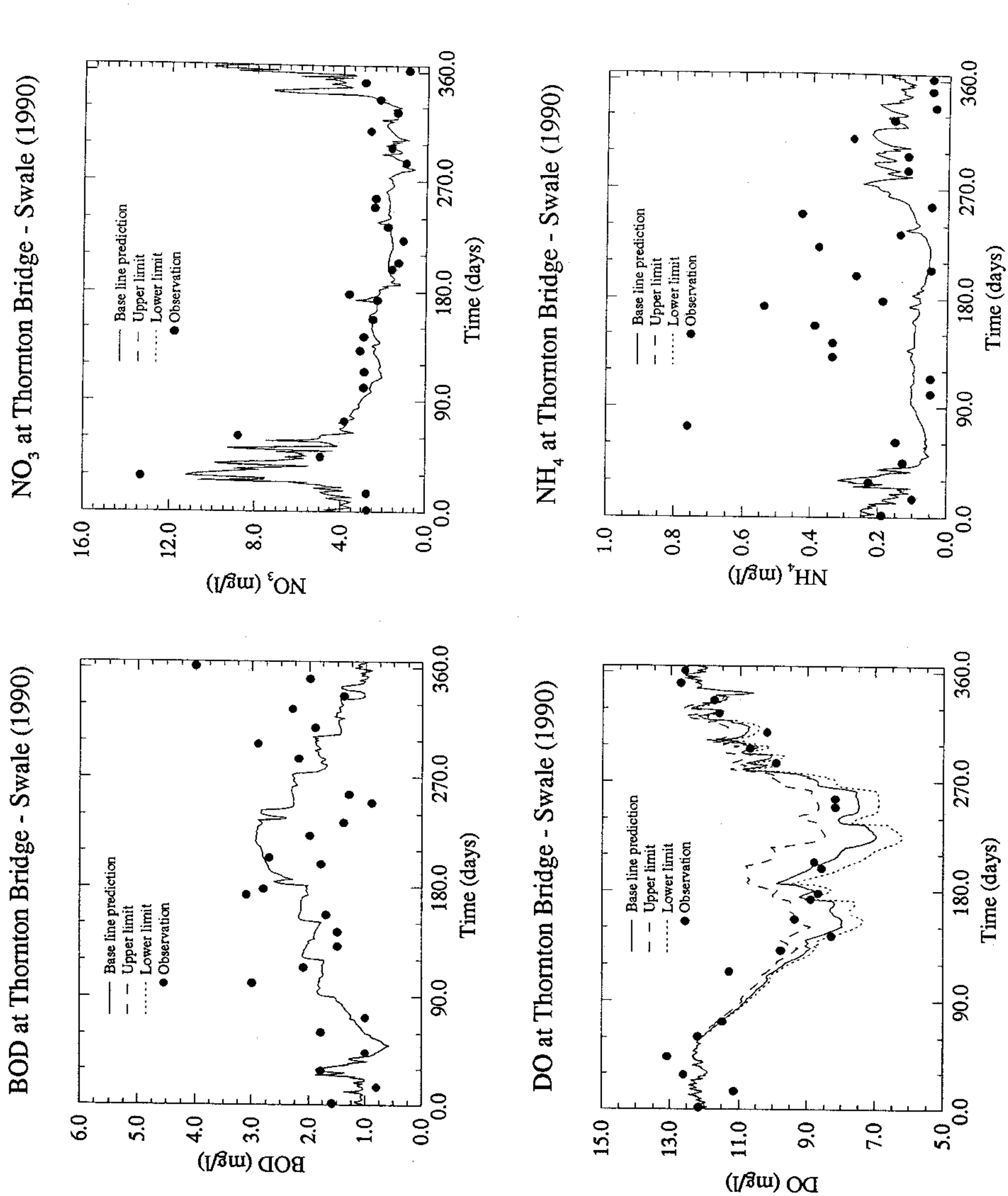


Figure 42 **Sensitivity analysis carried out on the River Swale data set: variation of both the photosynthetic oxygen production and respiration rate coefficients**

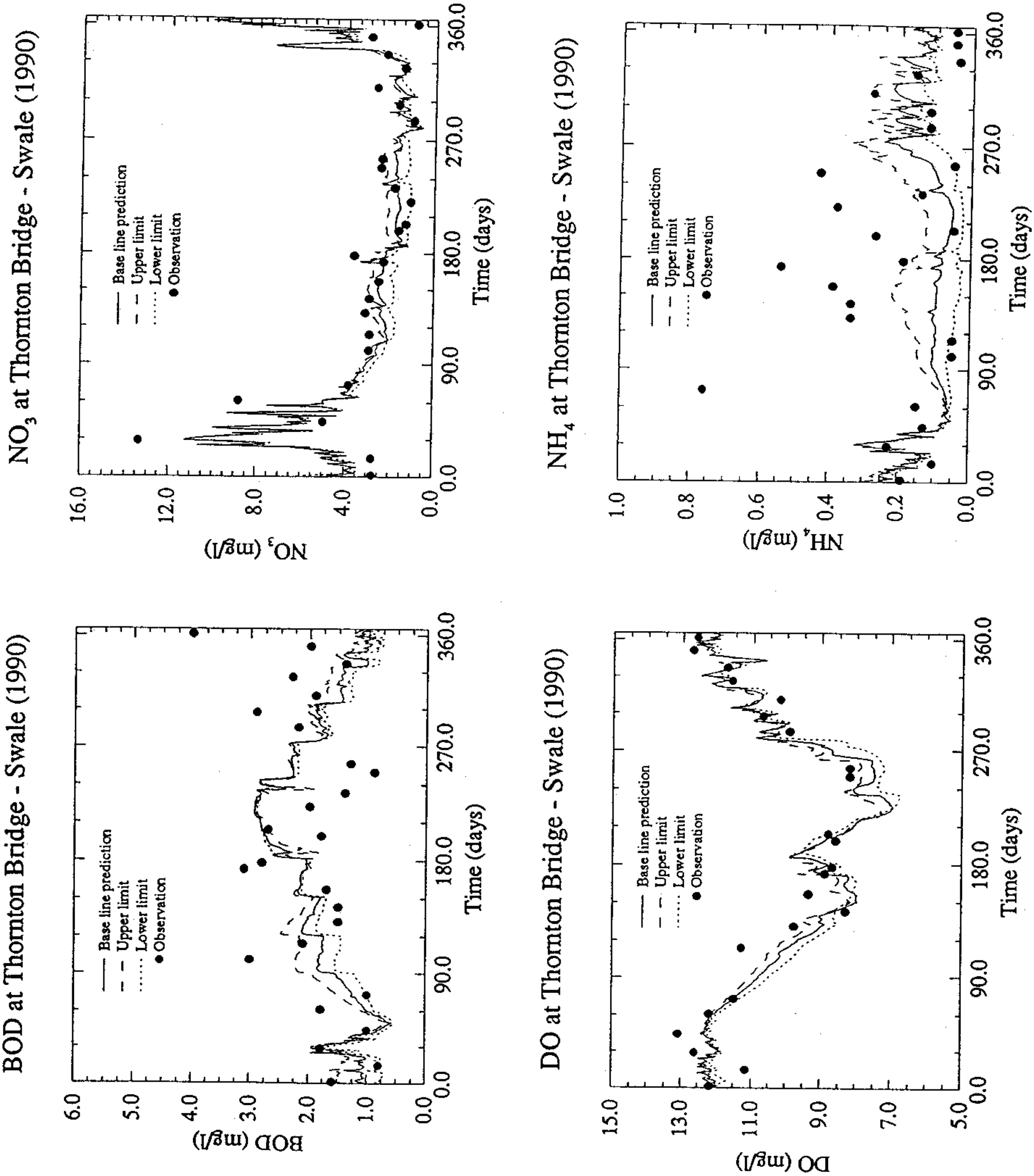


Figure 43 Sensitivity analysis carried out on the River Swale data set: variation of the b parameter in the QUASAR (V,Q) relationship

7 Validation

Through the calibration procedure carried out in Section 5, it was concluded that the behaviour of the Ouse catchment in 1990 can be reasonably well described in terms of the water quality determinands modelled by QUASAR. A number of problems were identified with the model, but overall the observed values of a basic set of conservative and DO-BOD determinands were simulated adequately. Furthermore, the model parameters selected in the calibration exercise were deemed to be either close to or within acceptable physical limits so that the rates of processes represented in the model, such as nitrification etc, are physically plausible.

These conclusions led to the next stage of model testing. Validation is carried out to test whether a model that has been calibrated for one set of data, can give a reasonable approximation of the behaviour observed in a second and independent set of data. If the model perfoms well against the independent set of data, a greater degree of confidence is given to future applications of the model with other data or indeed scenarios of change. The basic purpose of validation however is to ascertain if the assumptions or hypotheses that have been made about reality are invalid: it is never possible to completely validate a model as we can never prove that its results agree with reality in all respects. A knowledge of the invalid assumptions made for a model should lead to a revised and better approximation of reality.

In order to carry out a validation test, QUASAR has been applied to the Ouse catchment for the period 1/1/1991 to 31/10/1993. In setting up the data files for this simulation, exactly the same procedures as for the calibration phase were retained: the matching between gauged and ungauged tributaries was unchanged and daily inputs were estimated using the same methods, river and reach networks were not altered, and the reach parameters and rate coefficients were unchanged.

Figures 44 to 51 show the simulation results for the eight determinands (four to a page, conservative and non-conservative determinands shown on separate pages) at points in the river network corresponding to the major WQ site at the downstream point on each main river. The comparison is made against the observations at the appropriate WQ and NRA gauging sites. For ease of comparison with the earlier calibration results, the 1990 predictions and observations are also shown in the figures. The statistics given in these figures are for the complete period shown and not just for the three year validation period.

The conservative determinand predictions shown in all of these figures give good agreement with the four years of observed data. Noticeably the general trends of the observations such as the annual temperature variation, the flow peaks and base flows, the chloride peaks and base flow concentrations and the smaller annual pH variation are well predicted. An exception to this, is however the high chloride peak in early 1991 for the River Nidd at Skip Bridge. This may be explained by two measured chloride values (which may be an order of magnitude too high) for Coppice Beck during that time. Coppice Beck is the major matching station on this river and the large chloride concentrations were interpolated to produce a daily time series for the ungauged tributaries. This may suggest that a better method for defining inputs is required.

Another problem stemming largely from input definition is that pH values are generally lower than observed for the River Nidd (Figure 48). The reason for this has been explained previously as due to the lower pH values input from Gouthwaite reservoir. pH is at present treated as a conservative quantity in the model and this seems to be a good approximation for the other rivers in the Ouse catchment. Additionally, alkalinity (approximately equal to the sum of the bicarbonates of calcium, magnesium etc.) is probably a better conserved quantity than the hydrogen ion concentration and relationships between alkalinity and pH should be explored for possible inclusion in the model.

In considering the flow, the predicted falling limbs of the hydrographs have a tendency to drop more quickly than those observed. The base flow, however, is well predicted. The performance of the model in terms of its ability to yield a reasonable match to the non-conservative determinands is sensitive to the correct characterisation of the flow (Section 6.2.10). This sensitivity is due to the importance of residence time in the dynamics of a suspended biomass in a flowing system, especially in a dry year, where small changes at low flows can yield significant changes of residence time.

The observed non-conservative determinands show a greater variability than the conservatives due to the biochemical transformations occurring. These transformation rates are furthermore dependent upon temperature which is modelled conservatively. This introduces further complexities on the usual transport behaviour and makes non-conservative determinands more difficult to describe.

It is evident that nitrate predictions compare well with observations throughout the four years for each of the WQ sites, with both peak flow and base flow concentrations being well simulated. This is a gratifying result and indicates that the major processes affecting nitrate, i.e. nitrification and denitrification, are well represented in the model. Comparison of predicted ammonium concentrations with observations reveals that generally the base flow concentrations are reasonably well simulated as well as some of the peak flow concentrations. However, there is a greater degree of variability in the observations which is probably due to non-point sources and the interpolation method for inputs. Additional sources can be input into QUASAR by further discretisation of the network and by including them as point-like inputs when their magnitude and variability are known.

Dissolved oxygen is generally well predicted throughout the calibration and validation period, with the observed annual patterns described well by the model. The River Nidd predictions in the validation period are actually an improvement over those in the calibration period which had a substantial input of liquid oxygen during the summer of 1990, a drought period, to prevent serious water quality problems. On a few occasions during the summer the predicted DO drops to very low levels (especially in the Ure), these periods are generally due to low flows and high ammonium and BOD concentrations input from STWs. Unfortunately there are only a few observations during these periods from which to assess the predictions.

BOD observations are much more difficult to predict due to the physical influence of algae, other biological processes and sedimentation occurring in the river system. There is also some concern over the actual measurements of BOD concentrations, which are difficult to make and can introduce errors of uncertain magnitude. Generally the predictions of BOD are at best only adequate, being simply of the same magnitude as the observations. It is often difficult to distinguish a seasonal BOD pattern due to biological activity because of the inputs from STWs etc, but concentrations tend to be high during wet months and during algae periods. This determinand would be better described when a more accurate model of algal processes is included in QUASAR, although the precise relationship between BOD and algae is unclear.

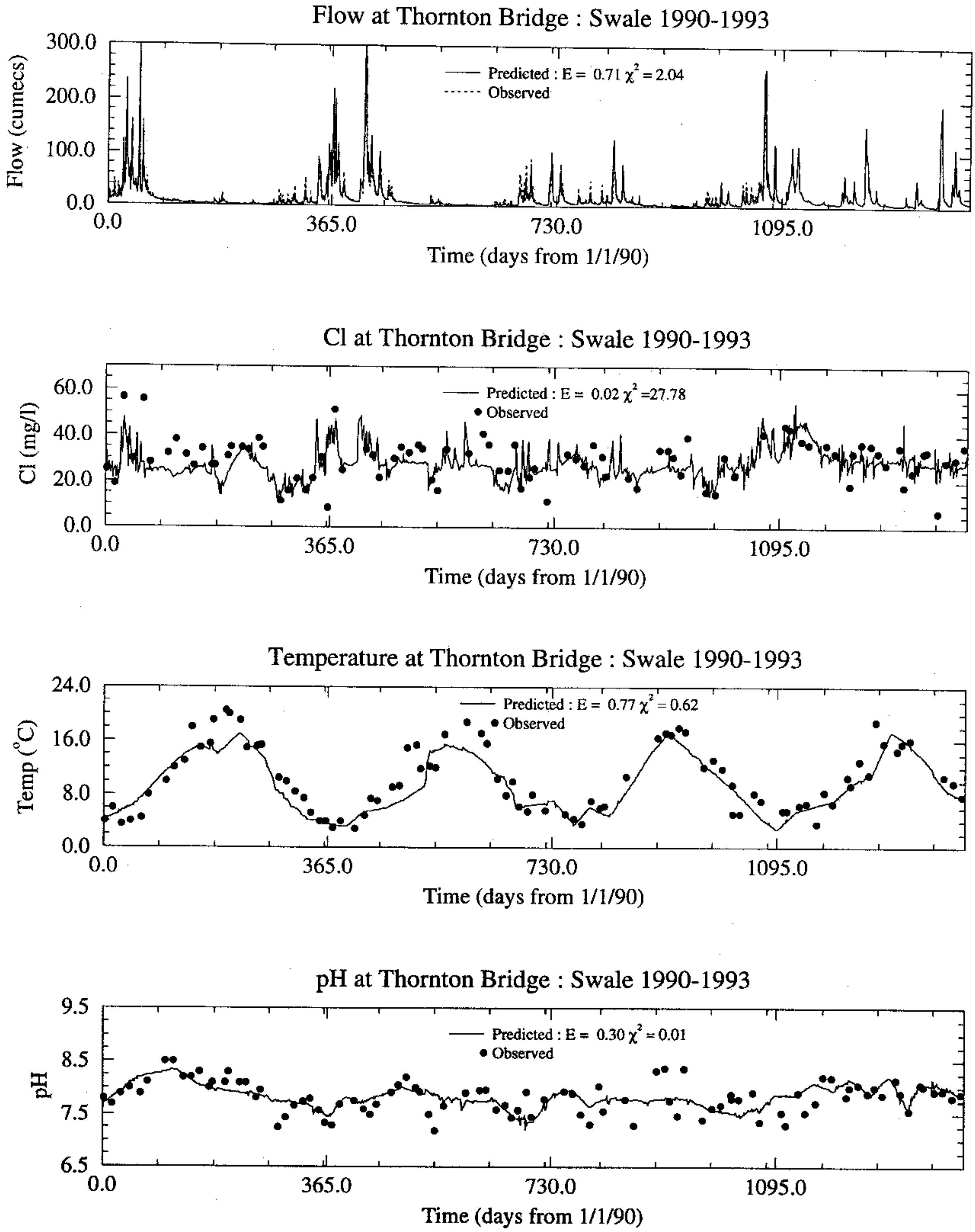


Figure 44 Validation plot for the River Swale at Thornton Bridge, 1990-94: conservative determinands.

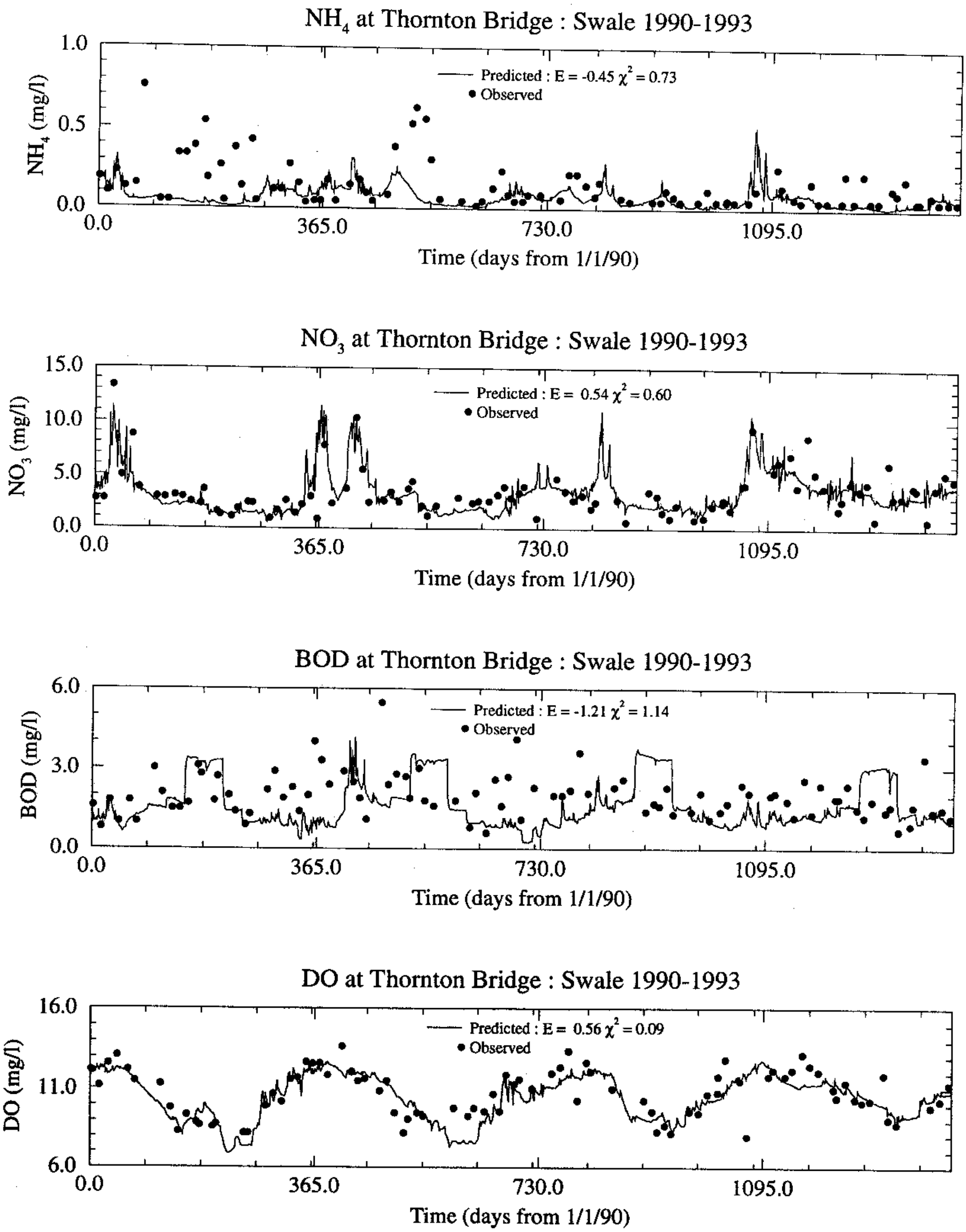


Figure 45 Validation plot for the River Swale at Thornton Bridge, 1990-94: conservative determinands.

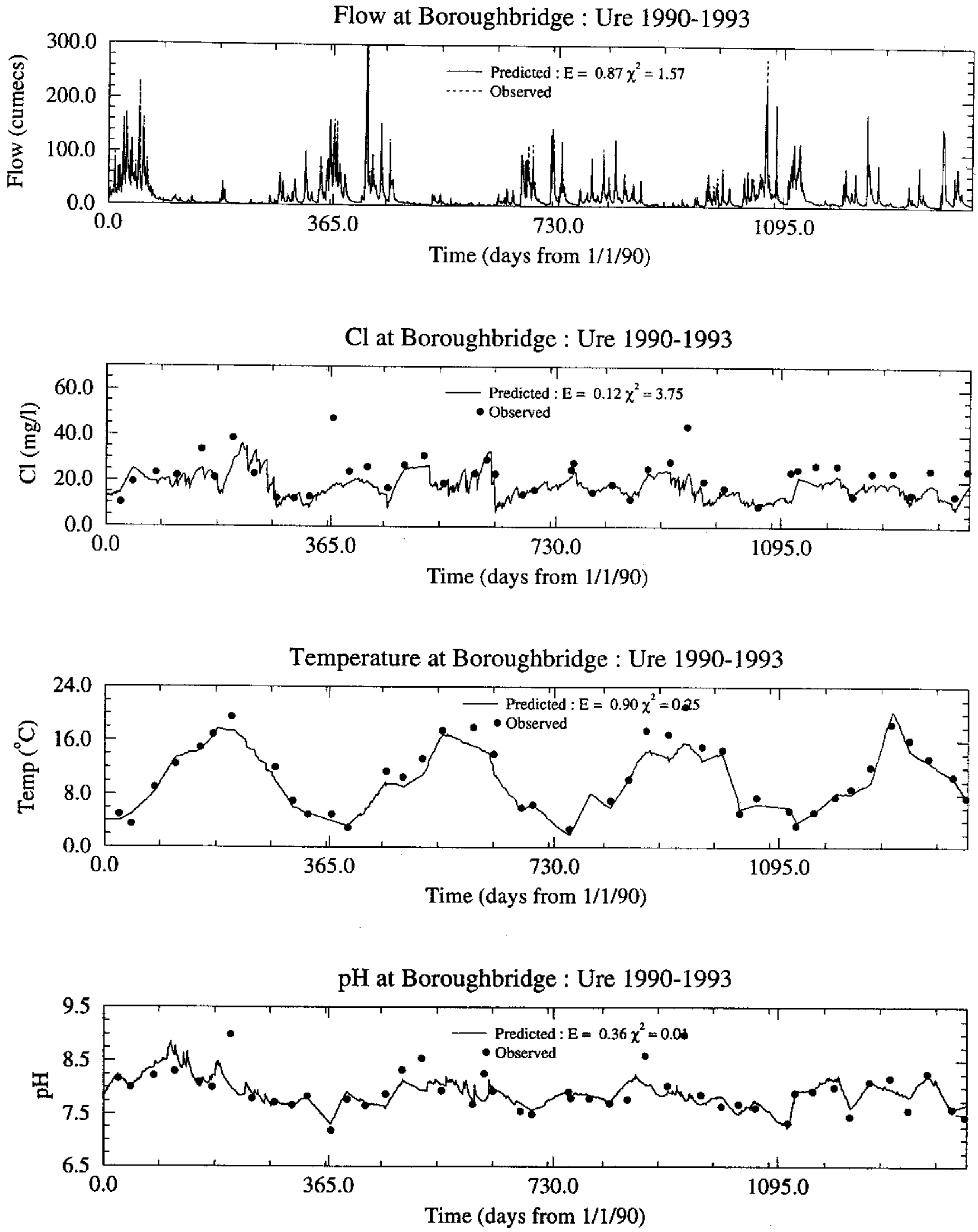


Figure 46 Validation plot for the River Ure at Boroughbridge, 1990-94: conservative determinands.

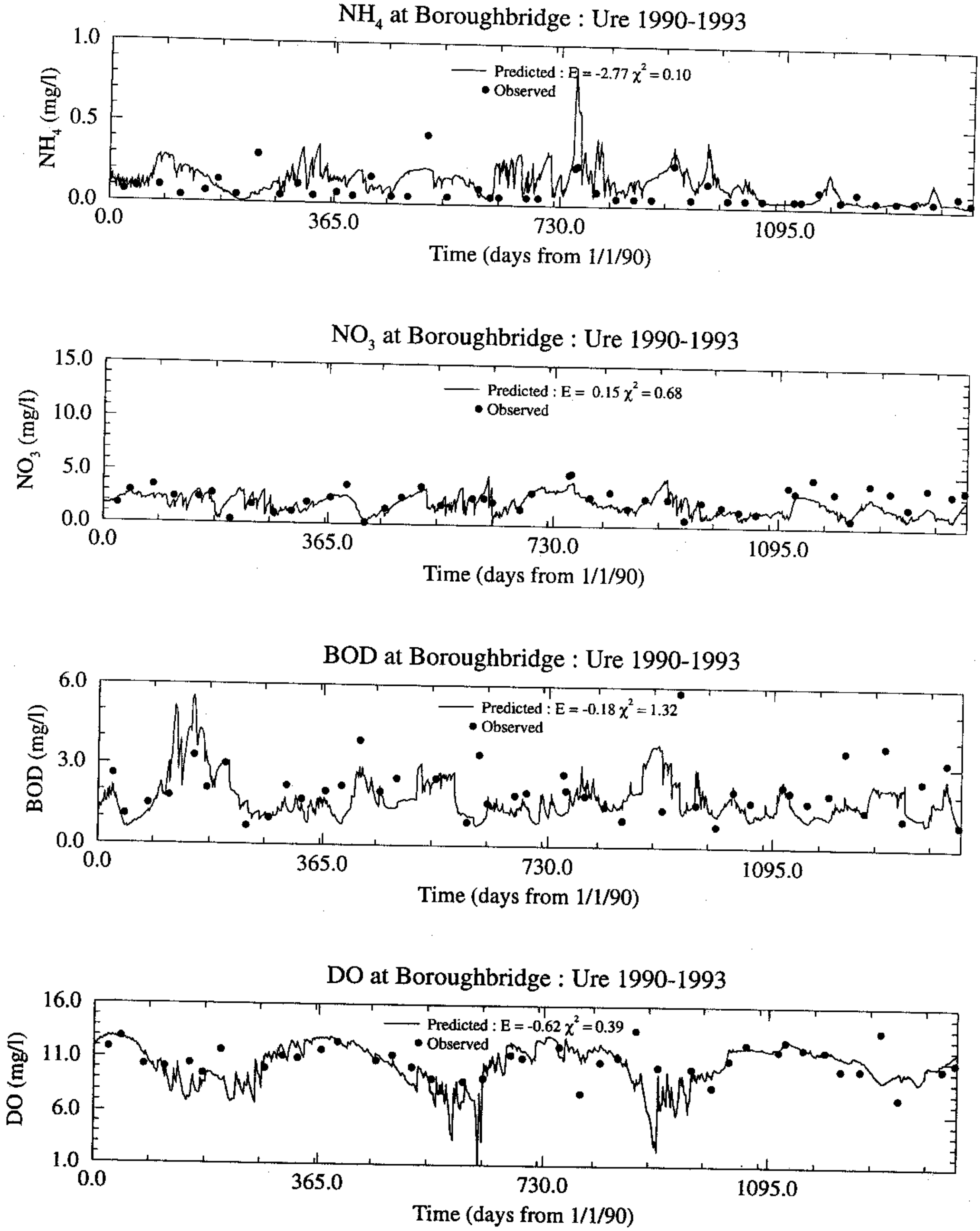


Figure 47 Validation plot for the River Ure at Boroughbridge, 1990-94: conservative determinands.

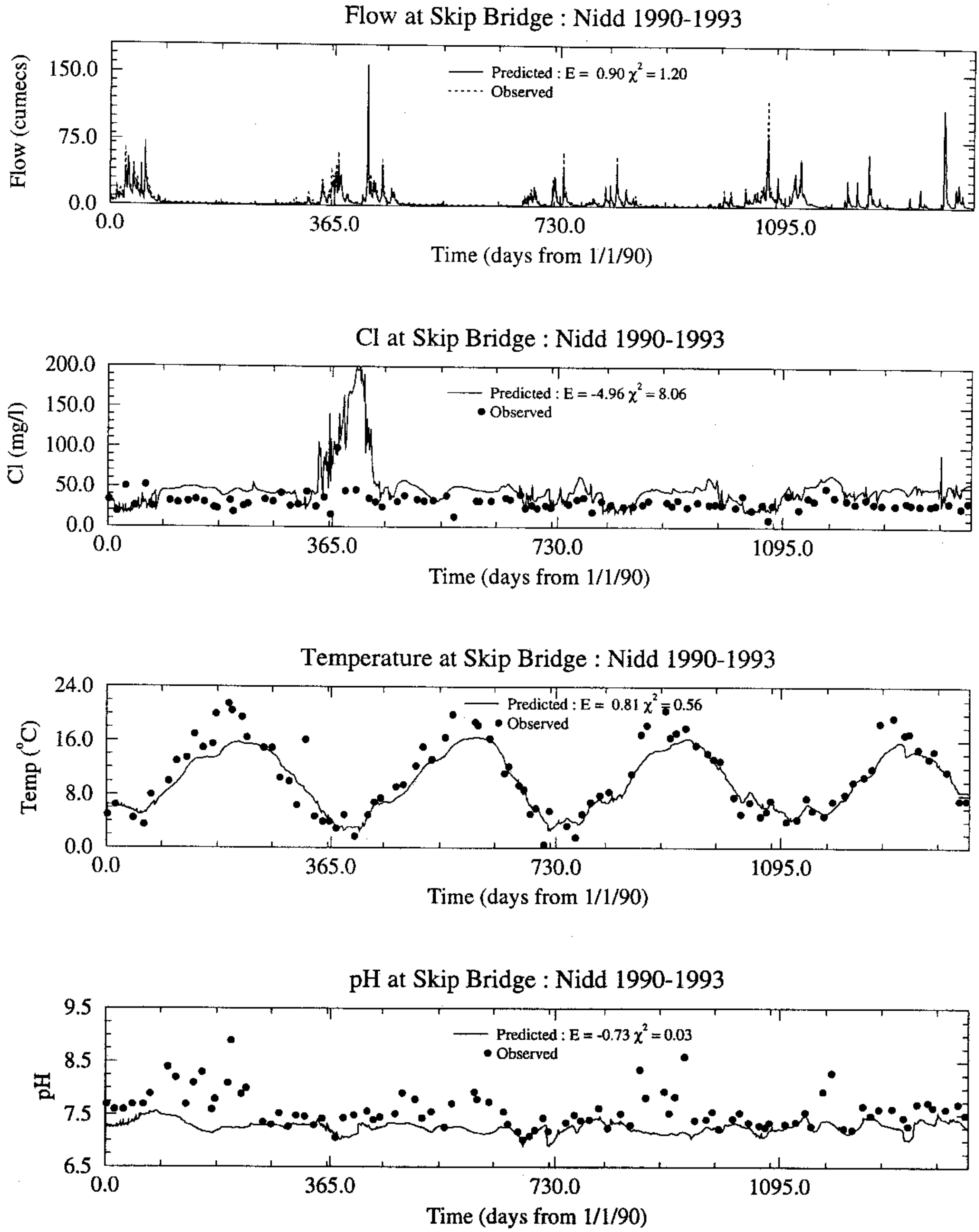


Figure 48 Validation plot for the River Nidd at Skip Bridge, 1990-94: conservative determinands.

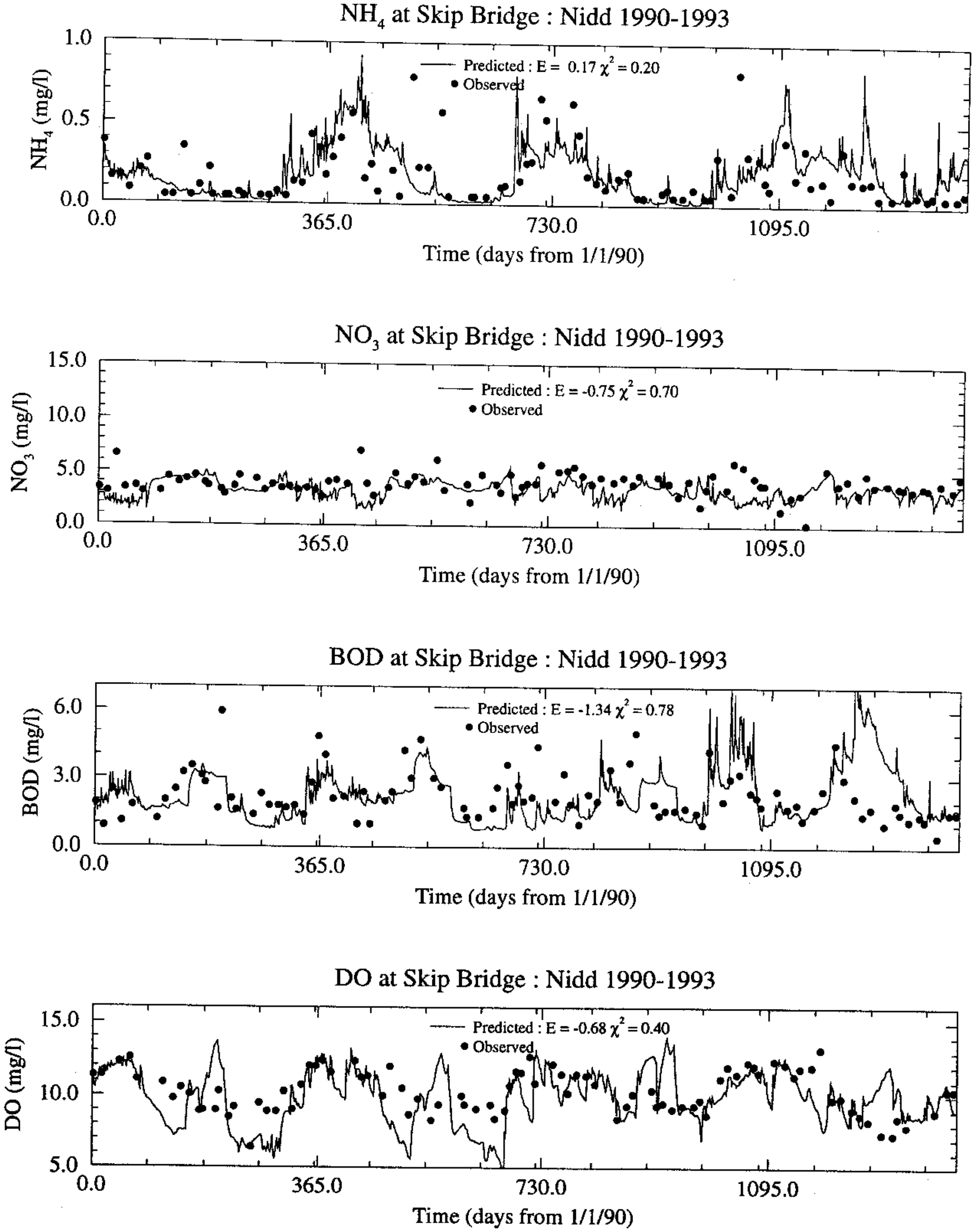


Figure 49 Validation plot for the River Nidd at Skip Bridge, 1990-94: conservative determinands.

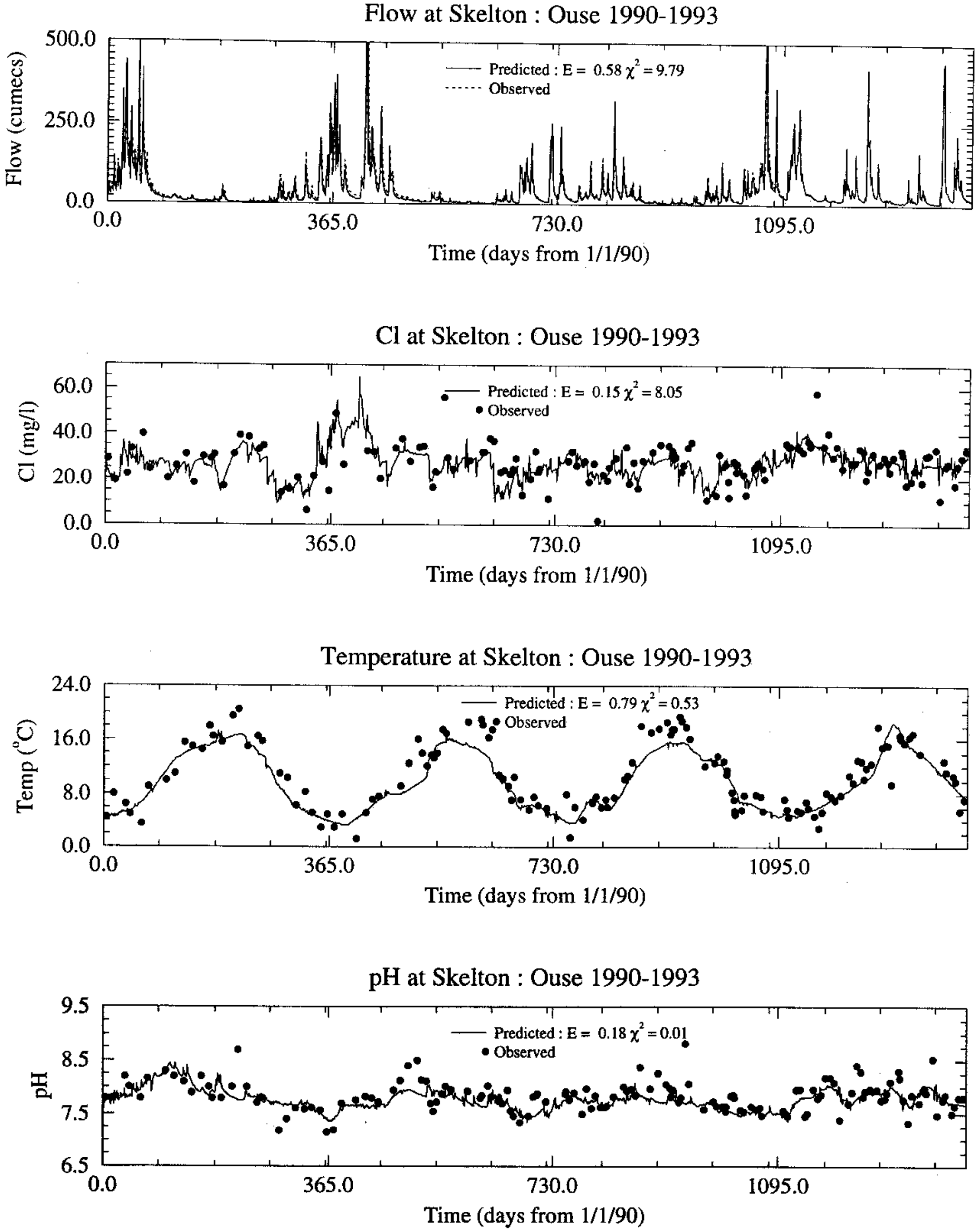


Figure 50 Validation plot for the River Ouse at Skelton, 1990-94: conservative determinands.

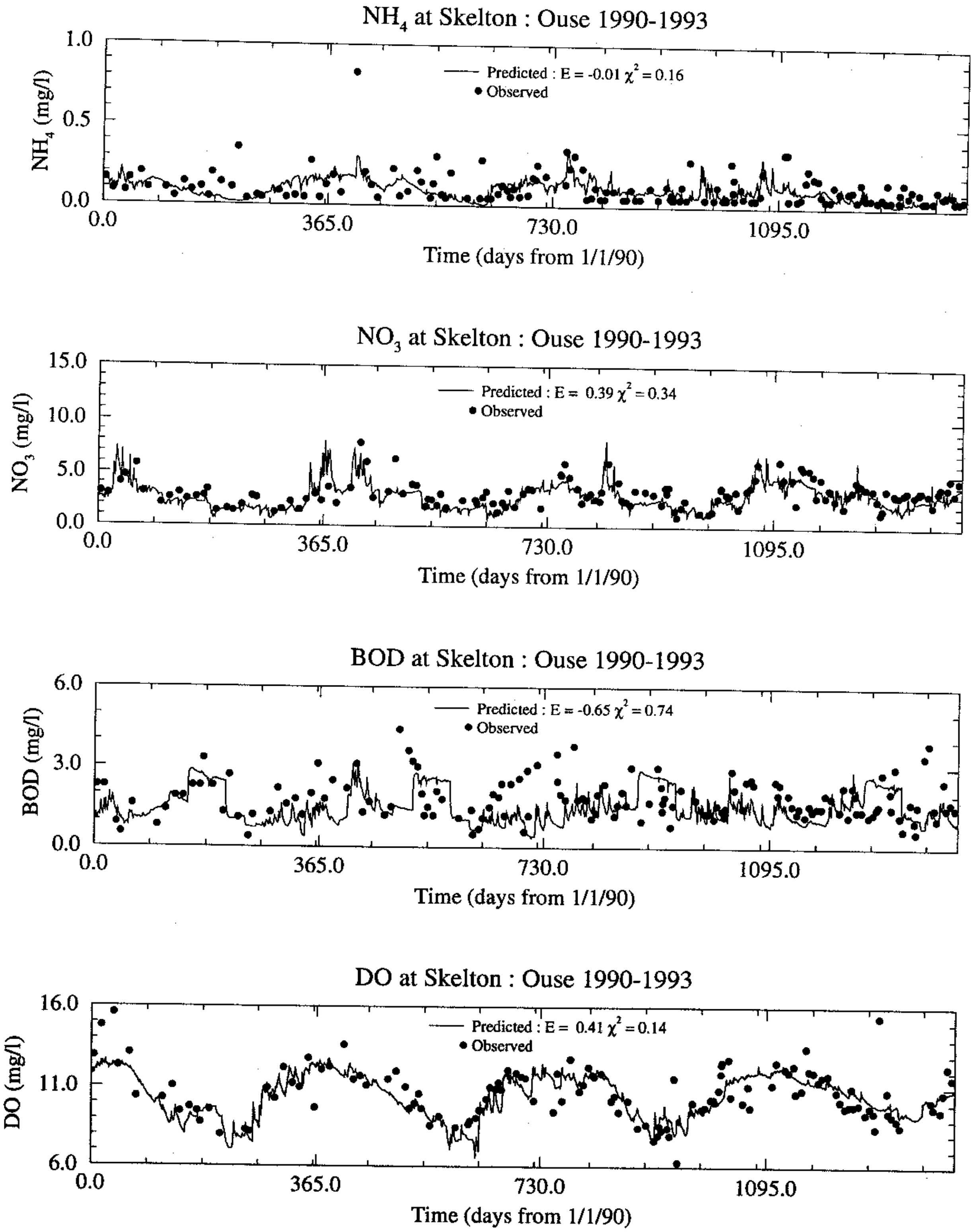


Figure 51 Validation plot for the River Ouse at Skelton, 1990-94: non-conservative determinands.

8 Conclusions

Generally dynamic models for DO-BOD interactions are not very easily calibrated and verified owing to the difficulties in obtaining data (Beck, 1975). In this work we are fortunate to have a great deal of data from NRA observations in the Yorkshire region, albeit on large time and space scales. These data have been successfully used within the IH WQ model QUASAR, which has a simple lumped-parameter differential equation representation of the major processes that affect the DO-BOD interactions in a river system.

The model has been applied to the relatively unpolluted Ouse catchment (area 3315 km^2) using only major point-source WQ inputs from STW and WPC works, gauged catchments and estimates of ungauged catchment tributary inflows. Discretising the Ouse catchment into a fairly large number of tributaries based on dynamic water balance considerations, has enabled the major chemical inputs into the system to be realised.

Chemical monitoring is generally carried out on a monthly basis, with fortnightly samples taken at the major downstream sites for each river. QUASAR is highly dependent upon its inputs and incorporating monthly observations in the modelling will broadly speaking, allow the major seasonal trend for that determinand to be simulated. The introduction of linearly interpolated daily values for WQ is an important component of the modelling procedure. QUASAR has been able to predict well the overall changes in WQ due to changing hydrological and seasonal circumstances.

The WQ input to each main river from a catchment is effectively the summation of all the inputs and processes occurring in that catchment. Including a large number of gauged and ungauged catchments as input to the model has thus effectively allowed the introduction of non-point source inputs into the modelling. However some non-point source chemical inputs into the Ouse system have not been identified in this work. This can be inferred from the WQ observations in the Vale of York (see figures in Section 5) where the influence of agricultural diffuse sources are presumably more evident.

Considering the accuracy and reliability of the quantification of the pollutant discharges and the contribution of diffuse sources, calibration and validation can be assumed to be successful for most of the determinands described by QUASAR. Only BOD consistently does not fall into this category.

Parameter values optimised for the calibration period are also appropriate for the validation period, even though the calibration period was an atypical drought year. This may indicate that the underlying model processes and the model parameterisation can correctly describe climate change scenarios such as changes in temperature and rainfall. Alternatively the ability of the model to simulate a drought and a normal year successfully with the same parameter set may be due to the calibration period being taken over the complete year. This effectively reduces the influence of low flows and higher temperatures during the summer period. The impact of climate change on river WQ using QUASAR was investigated by Jenkins et al. (1993), and it was concluded that the impact on river WQ, arising directly as a consequence of the change in climate was relatively small. It was further concluded that river WQ is far more sensitive to factors such as effluent disposal and the manner in which the water resource is managed.

A detailed analysis of the capabilities of the model has been carried out, and this work has revealed several areas requiring further development of the process representation in the model. It was identified that during low flow periods, directly after a large effluent discharge of ammonium and BOD the river conditions can show a considerable deleterious effect. Modifying the rate coefficient parameters so that ammonium and BOD predictions approximately follow the observations leads to depleted DO predictions. The river conditions usually return to "normal" levels several reaches downstream, due to the effect of dilution and natural rearation. In order to improve the simulation of the river conditions directly downstream of an effluent point the processes of uptake of ammonium by algae and bacteria need to be explicitly included in the model.

The work todate has centred on the application of a basic DO-BOD model to the Ouse system. The future requirements of LOIS are that a greater range of determinands such as phosphorus, algae, silica and trace metals etc need to be incorporated in the model. There is thus a need to understand the transport and associated transformations of these additional chemical and biological determinands within the river system. A further requirement is that the model is to be more reliant upon the nutrient loads and that the reach parameters are derived from a more fundamental physical basis.

It is proposed that algae modelling is first incorporated in QUASAR. This involves a more detailed study of the nutrient cycle within a river. Depending upon the degree of detail envisaged in modelling, the data requirements can be large, e.g. numbers of different types of algae and zooplankton species and knowledge of all nutrients - nitrogen, phosphorus, carbon and silicon etc are required as boundary conditions for the river. The usual way around this is to model chlorophyll-a which is a composite quantity representing algae since it is contained in all algal species. By lumping the algae species together in this way the representation of the nutrient cycle is dramatically simplified, but much detail is then lost. It is proposed that a more detailed model of algal growth is incorporated into the river model, based on the work of Canale et al., (1976), as this is thought to be necessary in order to model the above determinands adequately.

In order to apply a complex nutrient and algae model to a river network, a large amount of data is required for the model boundary conditions. To reduce the number of boundary conditions it is proposed that sub-catchments are characterised in terms of growth boxes or growth reaches. Algal growth in these boxes is determined by light and nutrient inputs and has a dynamic residence time calculated from the flow conditions and sub-catchment size. Calibration of these boxes is necessary at the sub-catchment outflows into the main river and this can be achieved by comparing predictions of chlorophyll-a totals with observations. Within LOIS, the Upper Swale catchment is monitored with a sufficient number of chlorophyll-a and nutrient measurements to allow an algal model to be calibrated. The chlorophyll-a measurements on the Lower Swale can be used to test the dynamic components of the model.

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APPENDIX 1 QUASAR MODEL EQUATIONS

The generalized equation for a water quality variable in QUASAR is given by

$$\frac{dX_j}{dt} = \frac{1}{TC}(X_{ij} - X_j) + \sum \text{sources} - \sum \text{sinks}$$

where X_j is the jth water quality variable and X_{ij} is the initial value of this variable. The time constant TC is given by;

$$TC = \frac{\ell}{V} = \frac{\ell}{bQ^c}$$

where ℓ is the length of the mixed tank reactor and V is the velocity of the flow determined by the empical relationship $V=bQ^c$ where Q is the discharge and b and c are empirical parameters.

FLOW

Flow is treated in QUASAR as a conservative quantity. The present version makes the assumption that flow is slowly varying. The form of the equation solved as a kinematic wave is given by

$$\frac{d(X_1)}{dt} = \frac{U_1 - X_1}{TC}$$

+ Tributory inputs

+ Effluent inputs

− Abstractions

where U_1 and X_1 are the input and output flows.

CONSERVATIVE

A conservative water quality variable has been included in QUASAR to allow the user to model any variable that, maybe as a first approximation, can be assumed to behave conservatively. The equation for a conservative variable is

$$\frac{d(X_3)}{dt} = \frac{U_3 - X_3}{TC}$$

where U_3 and X_3 are the input and output concentrations of a conservative water quality variable.

NITRATE

Two processes affect the rate at which the nitrate concentration changes in the water column. These are nitrification and denitrification. The differential equation describing the rate of change of nitrate concentration with time is given as

$$\frac{d(X_2)}{dt} = \frac{U_2 - X_2}{TC}$$

$-K_5.X_2$ denitrification

$+K_{15}.X_6$ nitrification

where U_2 and X_2 are the input and output nitrate concentrations, K_5 and K_{15} are the rate coefficients associated with the processes indicated and X_6 is the ammonium concentration. If the dissolved oxygen level goes to zero, then the term involving K_{15} is omitted as oxygen is required in order for the nitrification reaction to proceed.

The nitrification rate increases with increasing temperature following the relationship below

$$K_{15} = K_{15}^{0} \,.\, 10^{(0.0293T)}$$

where $K^0{}_{15}$ is the nitrification rate at 20°C in units of day^{-1} and in the range of 0.01 to 0.5, T is the temperature in °C.

Denitrification has the following temperature dependence

$$K_5 = K_5^0 \,.\, 1.0698 \,.\, 10^{(0.0293T)}$$

where $K^0{}_5$ is the denitrification rate at 20°C in units of day^{-1} and in the range of 0.0 to 0.5.

AMMONIUM

As has been described above, loss of ammonium occurs through oxidation to nitrate. In QUASAR this process is assumed to occur in one step and is modelled by the following differential equation

$$\frac{d(X_6)}{dt} = \frac{U_6 - X_6}{TC}$$

$-K_{15}.X_6$ nitrification

where U_6 and X_6 are the input and output ammonium concentrations and K_{15} is the nitrification rate.

AMMONIA

The concentration of ammonia is not actually produced as an output by the model, but it is computed from the ammonium concentration NH_4^+, pH and temperature data, and is given by

$$NH_3 = \frac{NH_4^+}{10^{(pKA-pH)}}$$

where pKA is given by

$$pKA = \frac{2754.9}{(T \cdot 273.15)}$$

DISSOLVED OXYGEN

The change in dissolved oxygen concentration is modelled as a result of photosynthetic O_2 production, benthic oxygen demand, reaeration (natural or due to the presence of a weir), nitrification, and loss due to BOD such that

$$\frac{d(X_4)}{dt} = \frac{U_4 - X_4 + WEIR}{TC}$$

$+P - R$	net algae O_2 contribution
$-K_4X_4$	benthic oxygen demand
$+K_2(CS - X_4)$	reaeration
$-4.43K_{15}X_6$	nitrification
$-K_1X_5$	loss due to BOD

where U_4 and X_4 are the input and output dissolved oxygen concentrations and K_i are the rate coefficients associated with the processes indicated. X_5 and X_6 are the BOD and ammonium concentrations respectively and WEIR is the increase or decrease in the oxygen concentration as a result of the river passing over a weir in the modelled reach. The change in the concentration is given by

$$WEIR = CS - \frac{(CS - XO_4)}{RT}$$

where CS is the oxygen saturation concentration, XO_4 is the dissolved oxygen above the weir and RT is the deficit ratio. The DO deficit ratio is an empirically determined function of the type of weir using a factor B, the pollution of the water (percent saturation) represented by A, the height from the top of the weir to the downstream water level H (m), and the temperature T (°C) of the water as shown below

$$RT = 1 + 0.38ABH(1 - 0.11H)(1 + 0.46T)$$

Photosynthetic oxygen production in river systems is described by the following relationship

$$P = K_8 (I^{0.79}\ 0.0317\, C\ell_a)\ (mg\ell^{-1}\text{-}day^{-1}) \quad - \quad \text{when } C\ell_a < 50\ (\mu g/\ell)$$

and

$$P = I^{0.79} (K_8 (0.0317 \times 50) + K_9\, 0.0317\, (C\ell_a - 50))\ (mg\ell^{-1}\text{-}day^{-1}) \ - \text{when } C\ell_a \geq 50\ (\mu g/\ell)$$

where $C\ell_a$ is the chlorophyll-a concentration ($\mu g/\ell$), and I is the solar radiation level at the earth's surface in watt hours per m^2 per day.

The two rates at which photosynthetic oxygen production occurs (K_8 and K_9) must be specified. Both K_8 and K_9 are functions of temperature;

$$K_8 = K_8^0\left((1.08)^{(T-20)}\right) \text{ and } K_9 = K_9^0\left((1.08)^{(T-20)}\right)$$

where $K^0{}_8$ and $K^0{}_9$ are the values of the rate coefficients at 20°C, and K_8^0 is usually in the range of 0.0 to 0.03 day^{-1}, and K_9^0 is in the range of 0.0 to 0.02 day^{-1}.

The loss of oxygen due to algae respiration is described by the equation

$$R = (0.14 + 0.013\, C\ell_a)\ 1.08^{(T-20)}\ (\mu g/\ell\text{-}day)$$

Oxygen is also lost by benthic oxygen demand (river bed or mud respiration) and this is described by the equation

$$M = K_4 X_4 \qquad \text{where} \qquad K_4 = K_4^0 . (1.08)^{(T-20)}$$

and $K^0{}_4$ is the value of the rate coefficient at 20°C and is usually in the range of 0.0 to 0.5 day^{-1}.

Oxygen is added to the system by the natural reaeration of the river at the surface. The reaeration rate is given by

$$\text{reaeration rate } (mg\ 0_2\ \ell^{-1}.day^{-1}) = K_2 (CS - X_4)$$

CS is the saturation concentration for DO defined as

$$CS = 14.652 - 0.41022T + 0.0079910T^2 - 0.000077774T^3$$

where T is the temperature in °C.

In QUASAR the temperature correction applied is given by

$$K_2 = \frac{5.316 \times V^{0.67} \times 1.024^{(T-20)}}{d^{1.85}}$$

where V is the stream velocity in ms^{-1} and d is the river depth in m.

BIOCHEMICAL OXYGEN DEMAND

Biochemical oxygen demand is a measure of the consumption of oxygen caused by the decay of organic matter (carbonaceous BOD) plus the oxygen consumed by the nitrification of ammonium (nitrogenous BOD). In QUASAR these processes are modelled separately. The nitrogenous BOD has already been described. The differential equation describing the rate of change of carbonaceous BOD concentration with time is given as

$\frac{d(X_5)}{dt}$	$= \frac{U_5 - X_5}{TC}$	
	$-K_1.X_5$	BOD decay
	$-K_{18}.X_5$	sedimentation
	$+K_{10}Cl_a$	BOD contribution by algae

where U_5 and X_5 are the input and output BOD concentrations and K_1, K_{10} and K_{18} are the rate coefficients associated with the processes indicated. If the dissolved oxygen level goes to zero, then the tem involving K_1 is omittede as oxygen is required for BOD decay to occur.

The temperature dependency of BOD decay is given by

$$K_1 = K_1^0 \, 1.047^{(T-20)}$$

where K^0_1 is the rate coefficient for the loss of BOD at 20°C in units of day^{-1} and is usually in the range of 0.0 to 2.0.

Loss of BOD can also occur by sedimentation. This occurs at a rate proportional to the amount of BOD present with an associated rate coefficient K_{18}, usually in the range of 0.0 to 2.0 day^{-1}. As algae die they contribute to the BOD. The rate of contribution is proportional to the product of the concentration of algae and the rate of BOD addition by dead algae K_{10}, usually in the range of 0.0 to 0.5 day^{-1}.

TEMPERATURE

Temperature is modelled as a conservative variable thus assuming that heat exchange at the surface is negligible.

$$\frac{d(X_7)}{dt} = \frac{U_7 - X_7}{TC}$$

where U_7 and X_7 refer to the input and output temperatures respectively.

pH

QUASAR models pH by assuming that H^+ is conservative thus;

$$\frac{d(X_9)}{dt} = \frac{U_9 - X_9}{TC}$$

where U_9 and X_9 are the input and output hydrogen ion concentrations.

APPENDIX 2 QUALITY CLASSIFICATION FOR FRESHWATER RIVERS AND CANALS

(System introduced by the former National Water Council in 1978)

River Class	Quality criteria	Remarks	Current potential uses
1A Good quality	Class limiting criteria (95 percentile) (i) Dissolved oxygen saturation greater than 80% (ii) Biochemical oxygen demand not greater than 3 mg/l (iii) Ammonia not greater than 0.4 mg/l (iv) Where the water is abstracted for drinking water, it complies with requirements for A2* water (v) Non-toxic to fish in EIFAC terms (or best estimates if EIFAC figures not available)	(i) Average BOD probably not greater than 1.5 mg/l (ii) Visible evidence of pollution should be absent	(i) Water of high quality suitable for potable supply abstractions and for all other abstractions (ii) Game or other high class fisheries (iii) High amenity value
1B Good quality	(i) DO greater than 60% saturation (ii) BOD not greater than 5 mg/l (iii) Ammonia not greater than 0.9 mg/l (iv) Where water is abstracted for drinking water, it complies with the requirements for A2* water (v) Non-toxic to fish in EIFAC (or best estimates in EIFAC figures not available)	(i) Average BOD probably not greater than 2 mg/l (ii) Average ammonia probably not greater than 0.5 mg/l (iii) Visible evidence of pollution should be absent (iv) Waters of high quality which cannot be placed in Class 1A because of the high proportion of high quality effluent present or because of the effect of physical factors such as canalisation, low gradient or eutrophication	Water of less high quality than Class 1A but usable for substantially the same purposes
2 Fair quality	(i) DO greater than 40% saturation (ii) BOD not greater than 9 mg/l (iii) Where water is abstracted for drinking water it complies with the requirements fro A3* water (iv) Non-toxic to fish in EIFAC terms (or best estimates if EIFAC figures not available)	(i) Average BOD probably not greater than 5 mg/l (ii) Similar to Class 2 of RPS (iii) Water not showing physical signs of pollution other than humic colouration and a little foaming below weirs	(i) Waters suitable for potable supply after advanced treatment (ii) Supporting reasonably good coarse fishers (iii) Moderate amenity value
3 Poor quality	(i) DO greater than 10% saturation (ii) Not likely to be anaerobic (iii) BOD not greater than 17 mg/l. This may not apply if there is a high degree of re-aeration		Waters which are polluted to an extent that fish are absent or only sporadically present. May be used for low grade industrial abstraction purposes. Considerable potential for further use if cleaned up

4 Bad quality	Waters which are inferior to Class 3 in terms of dissolved oxygen and likely to be anaerobic at times		Waters which are grossly polluted and are likely to cause nuisance.

Notes (a) Under extreme weather conditions (eg flood, drought, freeze-up), or when dominated by plant growth, or by aquatic plant decay, rivers usually in Class 1, 2 and 3 may have BODs and dissolved oxygen levels, or ammonia content outside the stated levels for those Classes. When this occurs the cause should be stated along with analytical results.

(b) The BOD determinations refer to 5 day carbonaceous BOD (ATU). Ammonia figures are expressed as NH_4.

(c) In most instances the chemical classification given above will be suitable. However, the basis of the classification is restricted to a finite number of chemical determinands and there may be a few cases where the presence of a chemical substance other than those used in the classification markedly reduces the quality of the water. In such cases, the quality classification of the water should be down-graded on the basis of biota actually present, and the reasons stated.

(d) EIFAC (European Inland Fisheries Advisory Commission) limits should be expressed as 95 percentile limits.

* EEC category A2 and A3 requirements are those specified in the EEC Council Directive of 16 June 1975 concerning the Quality of Surface Water Intended for Abstraction of Drinking Water in the Member State.