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A COMPARISON OF WATER QUALITY MODELS OF THE AEROBIC NITROGEN CYCLE

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PREFACE

This paper is a contribution within the framework of Task 2 of the IIASA research area, *Resources and Environment*. Task 2 is broadly concerned with *Models for Environmental Quality Control and Management*, including hydrophysical and ecological models for water quality in lakes, reservoirs and river systems.

This study was carried out by the writer as a guest scholar at IIASA, during his sabbatical leave from M.I.T. in the period September, 1977, through January, 1978. The writer is indebted to the many IIASA staff members and guest scholars with whom he has discussed the philosophy and practice of water quality modelling during this period. In particular, he would like to express his appreciation for helpful suggestions to Professor Oleg Vasiliev, Deputy Director of IIASA and Head of the Resources and Environment Area; Dr. Alexander Leonov, Dr. Bruce Beck, Professor Sven Jørgensen; and to his former students, Dr. Masataka Watanabe and Dr. Mark Markofsky, who were at IIASA during a portion of this study.

Special thanks are due to Mr. Serge Medow, who programmed the mathematical models and generated the computer plots in a very efficient manner.

SUMMARY

The objective is to compare a sequence of biochemical water quality models of increasing complexity and diversity, in order to determine the level of complexity needed for predictive models. Primary consideration will be given to models simulating chemical, bacterial and algal components that can be compared with laboratory data.

The aerobic nitrogen cycle containing seven chemical and biological components of nitrogen is chosen for the comparative study. The nitrogen components can be coupled by various linear and/or non-linear transformation functions representing mineralization and oxidation of organic nitrogen and phytoplankton-zooplankton interactions.

Results of simulation runs for batch systems are compared with the same data. It is concluded that the non-linear couplings, representing bacterially mediated and plankton reactions, have a significant influence on both the system dynamics and the steady state nitrogen concentrations. Future research directions for comparative model studies are indicated.

TABLE OF CONTENTS

1. Introduction

One of the most difficult problems in the development of predictive water quality models is the determination of the appropriate degree of model complexity. A necessary, but not sufficient, condition for a predictive water quality model is that it be capable of simulating prior conditions observed during a certain time interval. The adjustment of model parameters to fit the observed data during this time interval is called "calibration". If a second set of observations, covering a different time interval, are available and if the model is capable of simulating these conditions without recalibration, the model has a certain claim to being predictive. At this stage the model is usually said to have been "verified". The latter is a subjective judgement since it depends on the degree to which the data and inputs used in verification differ from the data on which the model calibration was performed and on the predictive goals of the specific study.

The term "predictive water quality model", as used here, implies a deterministic model based upon hydrophysical and ecological knowledge as opposed to the fitting of regression equations which can easily satisfy the necessary calibration condition. When a model is called upon to predict water quality conditions not contained within the historical data base, one can have little confidence in regression equations as predictive tools.

The degree of complexity of a deterministic water quality model represents a compromise between the reality of nature and the abstraction of a mathematical model. The components of a water quality model may be grouped into the following categories:

(i) hydrothermal transport and mixing

(ii) chemical compounds

(iii) bacteria

(iv) plankton

(v) macrophytes and the higher biological trophic levels.

The order of listing of the components approximately corresponds to a scale of decreasing knowledge and ability to represent the processes in a deterministic manner. Thus, the question of model complexity should be considered in relation to the state of knowledge of the component process. In other words, there may be good justification for including in a model a significant degree of complexity in the first three component categories, involving hydrothermal, chemical and bacterial processes, than in the higher biological level components. A model structured in this manner has a number of advantages over a potentially simpler model employing a uniform degree of complexity among the various component categories.

The multi-level complexity model has the advantage of being able to make use of existing scientific knowledge of certain transformation rates, and more importantly, the same model can be used for the analysis of both laboratory and field data. When the laboratory tests (e.g. in a chemostat) are conducted using water from the lake or river under study, a number of important model parameters can be determined with good accuracy. It is of course recognized that not all component processes can be reproduced or simulated in the laboratory. However, those most susceptible to laboratory study are the hydrothermal, chemical and bacterial processes. Thus, in the model calibration phase, attention can be directed to those rate constants corresponding to the higher biological levels. This can be a significant advantage in water quality models involving many rate constants where formal parameter estimation and calibration techniques are difficult to apply.

A somewhat different approach to determining the appropriate degree of complexity has been proposed by Jørgensen et al (1977). Their method is based on calculating the effect of increasing the number of state variables

on the "ecological buffer capacity" of the system. Because of the importance of the question of model complexity, it is hoped that other investigators will be encouraged to express their views on this subject.

In the following section an attempt will be made to illustrate some of the ideas presented above. A sequence of existing biochemical water quality models of increasing complexity and diversity will be presented and compared with the same data sets. Primary consideration is given to models that simulate chemical, bacterial and planktonic transformations in various ways. Only components of the aerobic nitrogen cycle will be considered.

2. The Aerobic Nitrogen Cycle

The components of the aerobic nitrogen cycle considered in this study are shown in Fig. 1. They include the nitrogen in the chemical compounds of ammonium (N_1), nitrite (N_2) and nitrate (N_3); the nitrogen content of phytoplankton (N_4) and zooplankton (N_5); and particulate (N_6) and dissolved (N_7) organic nitrogen. Not included is free nitrogen and exchange of nitrogen between the atmosphere and bottom sediments. In the schematic diagrams illustrating the sequence of models that follows, the relative position of the "boxes" representing the components of the nitrogen cycle will be kept in the same positions as shown in Fig. 1. In order to emphasize the dynamics of the biochemical process the models will simulate fully mixed batch systems.

2.1 Oxidation of Inorganic Nitrogen

Models 1, 2 and 3 deal only with the nitrification sub-cycle in which ammonium (NH_4) is oxidized to nitrite (NO_2) and nitrate (NO_3). The three models are compared with laboratory data of Knowles et al (1965) using Thames River water.

Model 1 assumes that ammonium is converted directly to nitrate with a first order rate constant, as shown in Fig. 2. The equations for the batch system

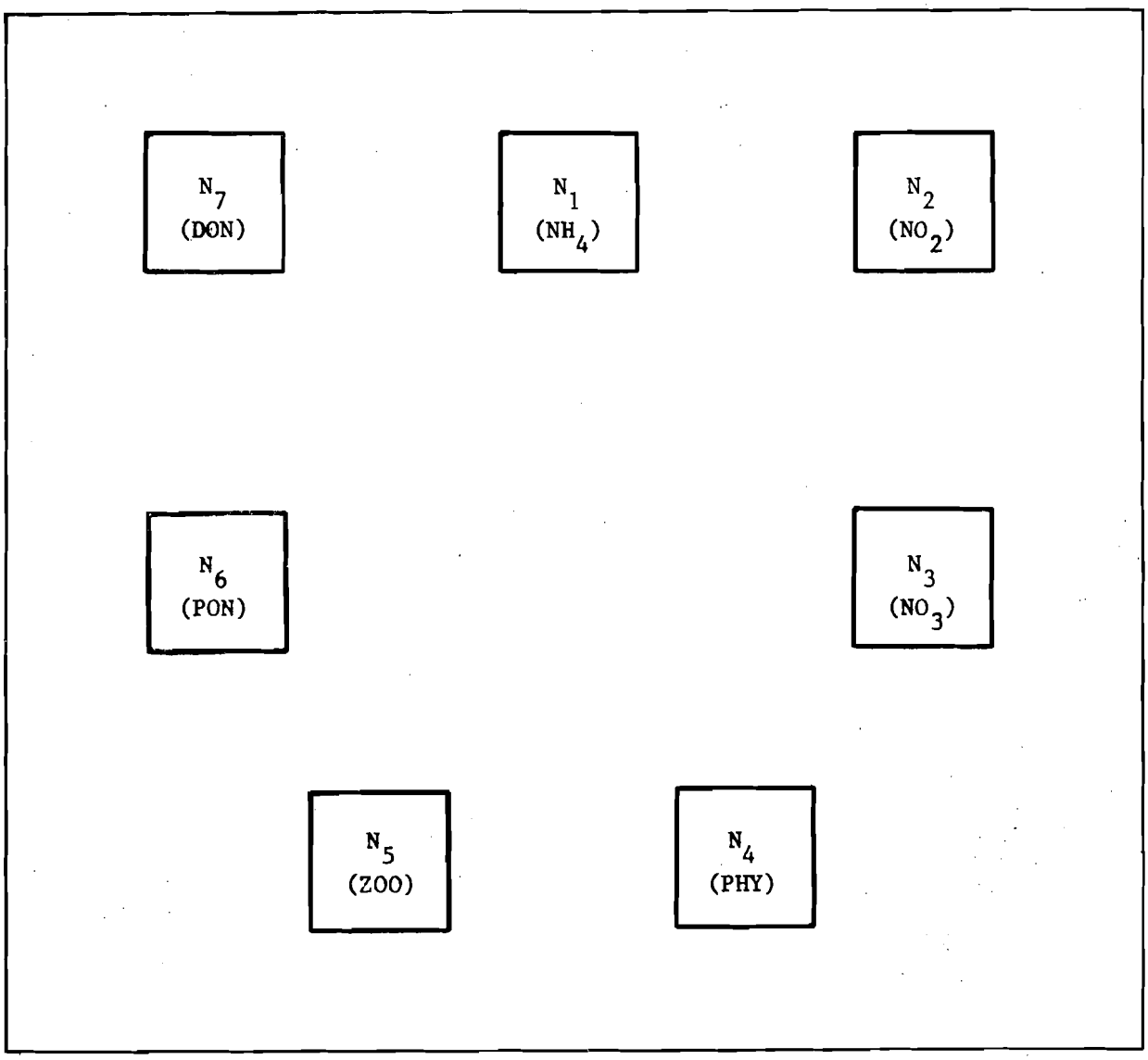

Fig. 1: Components of the Aerobic Nitrogen Cycle

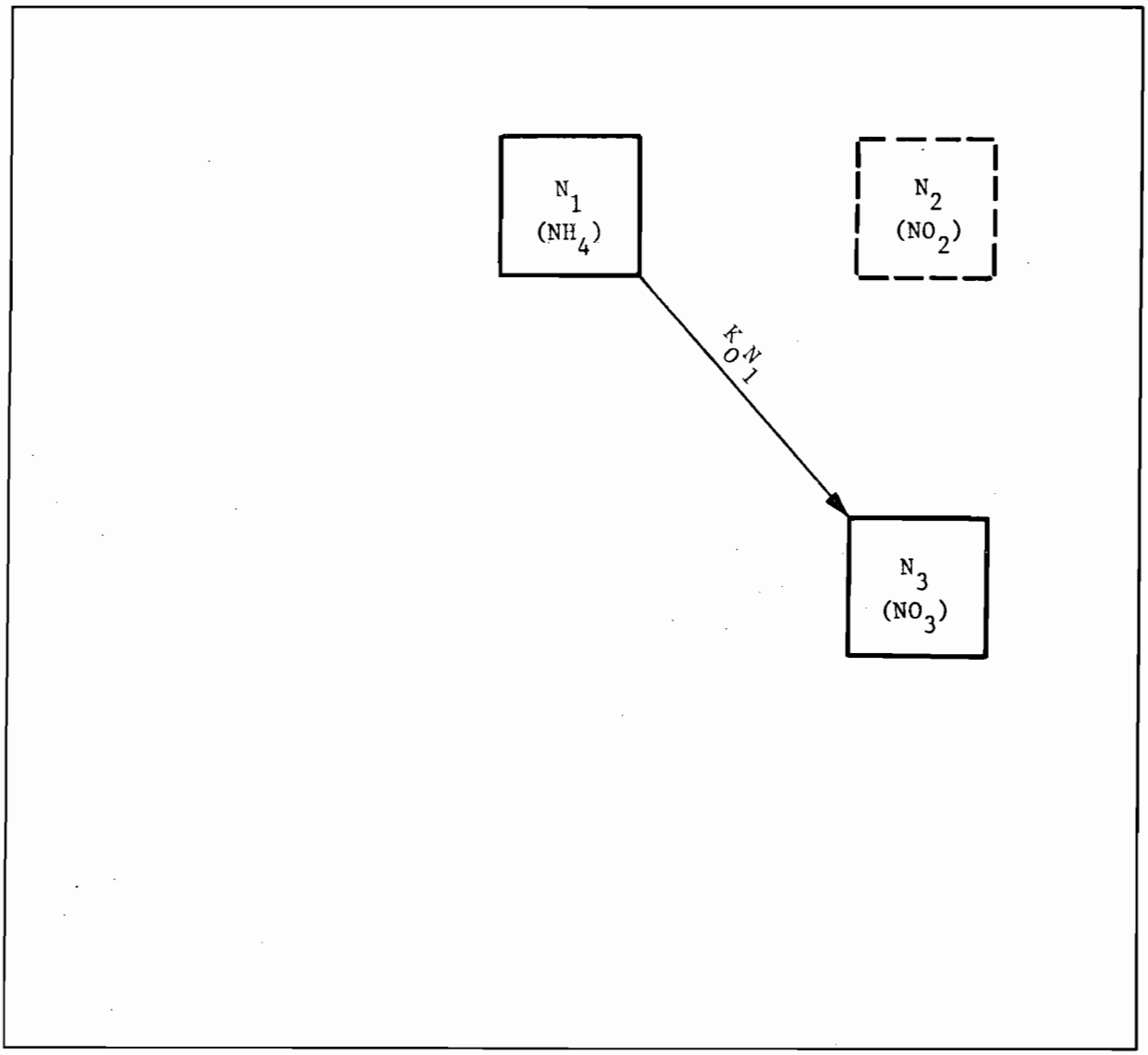

Fig. 2: MODEL 1 - First order Oxidation of Ammonium to Nitrate

are,

$$\underline{\text{MODEL 1:}} \quad \frac{dN_1}{dt} = -K_0 N_1 \tag{1}$$

$$\frac{dN_3}{dt} = K_0 N_1 \tag{2}$$

The model has one rate constant (K_0) and two initial values (N_{10} = 17.5 mg/l and N_{30} = 0). The solutions to equations (1) and (2),

$$\frac{N_1}{N_{10}} = e^{-K_0 t} \tag{3}$$

$$\frac{N_3}{N_{10}} = 1 - e^{-K_0 t} \tag{4}$$

are plotted in Fig. 3 in comparison with the data. Since the model does not contain the intermediate nitrite form, this portion of the data was omitted from the plot. The rate constant $K_0 = 0.16\ \text{day}^{-1}$ was chosen so as to approximately fit the data at $N_1/N_{10} = N_3/N_{10} = 0.5$. It is readily seen that the dynamics of the nitrification process are not well represented by a single rate constant model.

Model 2 simulates the formation of the intermediate nitrite (NO_2) with first order rate constants for both stages of the oxidation, as shown in Fig. 4. The equations are

$$\underline{\text{MODEL 2:}} \quad \frac{dN_1}{dt} = -K_1 N_1 \tag{5}$$

$$\frac{dN_2}{dt} = K_1 N_1 - K_2 N_2 \tag{6}$$

$$\frac{dN_3}{dt} = K_2 N_2 \tag{7}$$

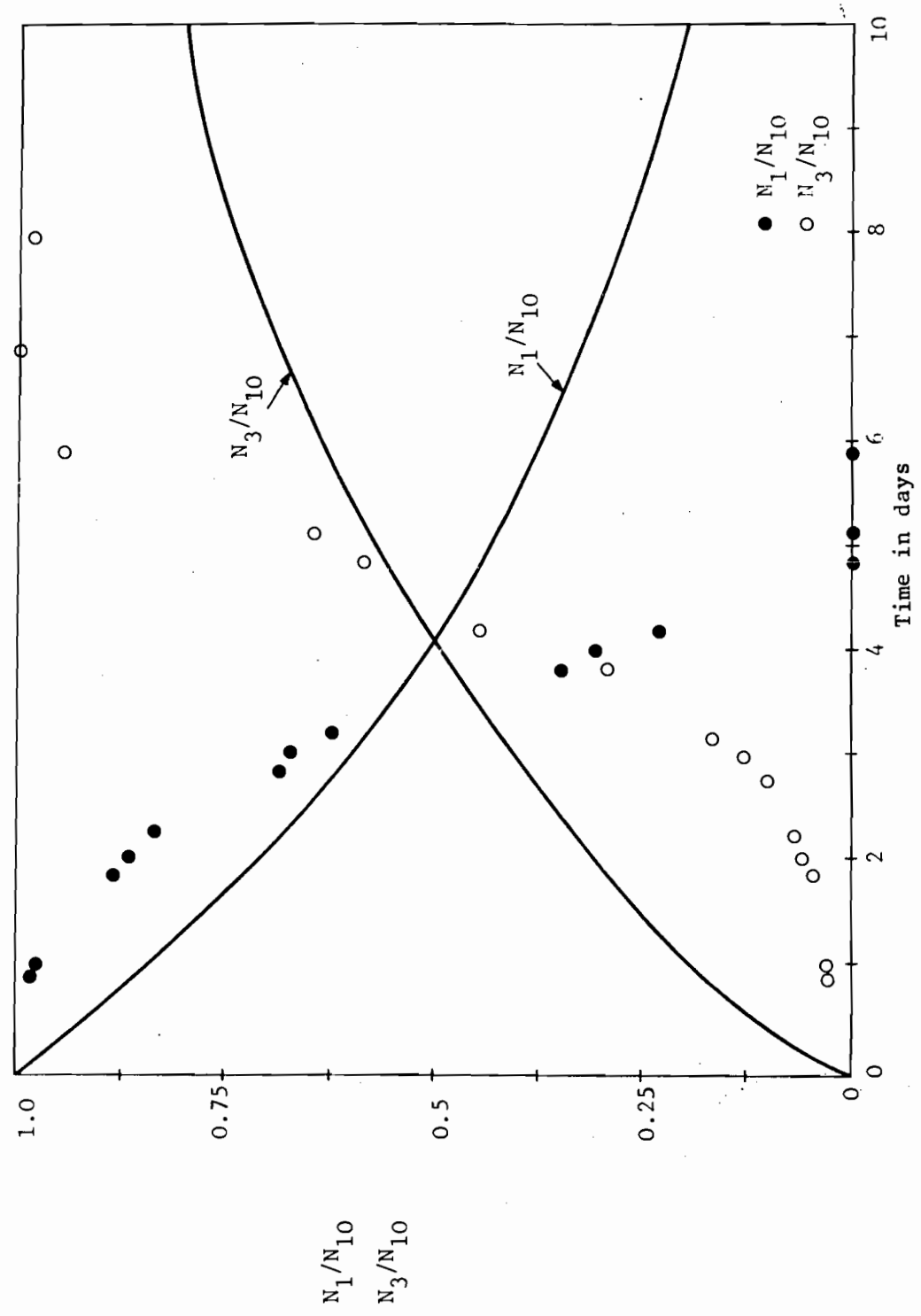

Fig. 3: Comparison of Model 1 with Data of Knowles et al (1965): $K_0 = 0.16\ day^{-1}$; $N_{10} = 17.5\ mg/l$; $N_{30} = 0$

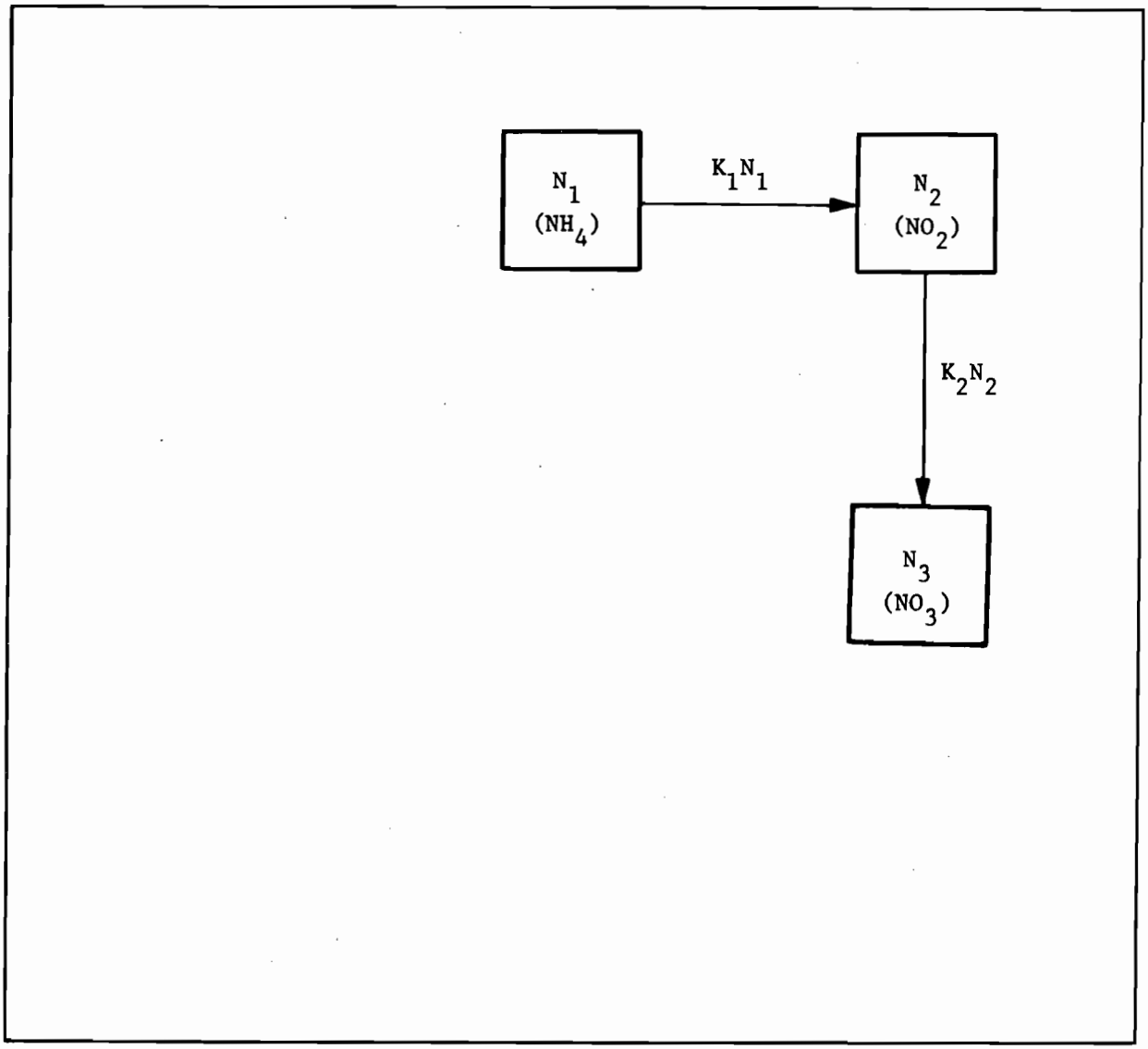

Fig. 4: MODEL 2 - First order Oxidation of Ammonium to Nitrite and Nitrate

Model 2 has two rate constants (K_1 and K_2) and three initial values (N_{10} = 17.5 mg/l and $N_{20} = N_{30} = 0$). The solutions to equations (5), (6) and (7),

$$\frac{N_1}{N_{10}} = e^{-K_1 t} \tag{8}$$

$$\frac{N_2}{N_{10}} = \frac{K_1 e^{-K_1 t} - K_1 e^{-K_2 t}}{K_2 - K_1} \tag{9}$$

$$\frac{N_3}{N_{10}} = 1 - \frac{K_2 e^{-K_1 t} - K_1 e^{-K_2 t}}{K_2 - K_1} \tag{10}$$

are plotted in Fig. 5 in comparison with the data. The rate constants $K_1 = 0.16$ day^{-1} and $K_2 = 0.28$ day^{-1} were chosen to fit ammonium at $N_1/N_{10} = 0.5$ and to match the time at which the peak concentration of nitrite occurs, i.e. (N_2/N_{10}) max. at 4.5 days. Other combinations of K_1 and K_2 were tried; however, none of them overcame the overall lack of agreement with the data.

Model 3 recognizes, as did Knowles et al (1965), that the oxidation of ammonium is bacterially mediated; specifically, that nitrosomonas and nitrobacter are responsible for the two oxidation stages shown in Fig. 6. The conservation of mass equations for the three nitrogen components and the two bacteria are expressed in terms of Michaelis-Menten kinetics,

MODEL 3:
$$\frac{dN_1}{dt} = -\frac{\hat{\mu}_1}{Y_1}\left(\frac{N_1}{K_{s1} + N_1}\right)X_1 \tag{11}$$

$$\frac{dN_2}{dt} = \frac{\hat{\mu}_1}{Y_1}\left(\frac{N_1}{K_{s1} + N_1}\right)X_1 - \frac{\hat{\mu}_2}{Y_2}\left(\frac{N_2}{K_{s2} + N_2}\right)X_2 \tag{12}$$

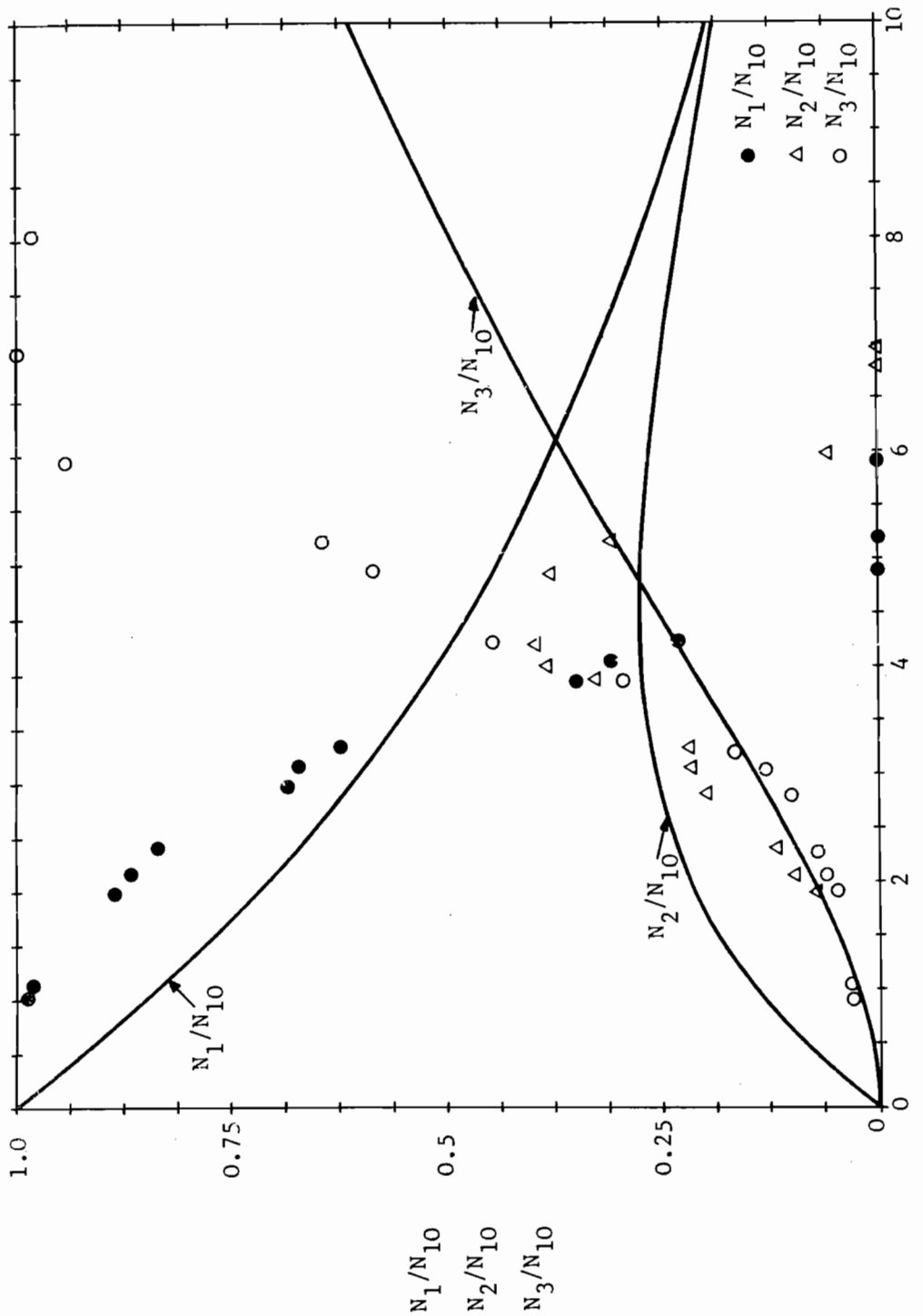

Fig. 5: Comparison of Model 2 with Data of Knowles et al (1965):

$K_1 = 0.16\ day^{-1}$; $K_2 = 0.28\ day^{-1}$;

$N_{10} = 17.5\ mg/l$; $N_{20} = N_{30} = 0$

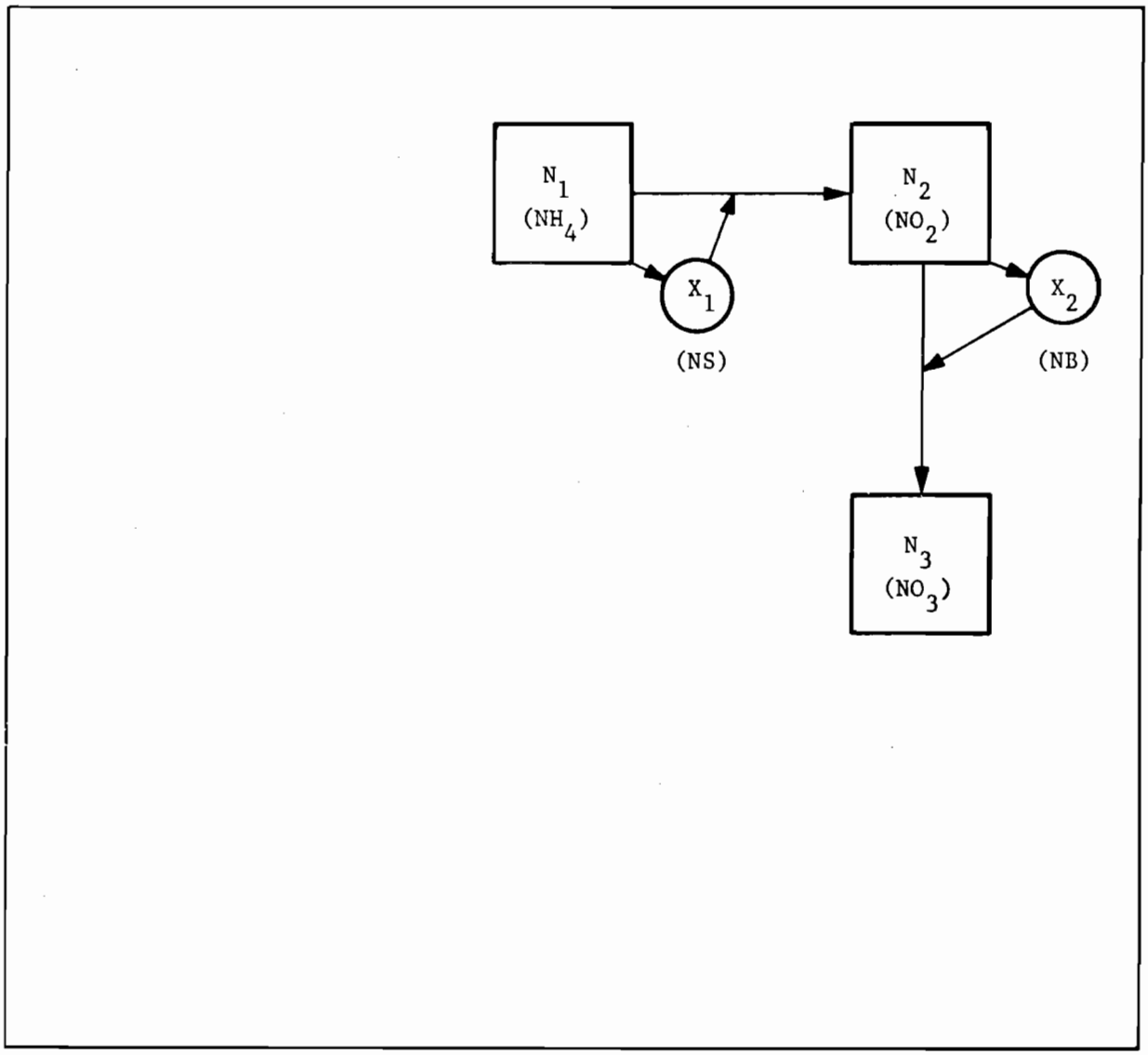

Fig. 6: MODEL 3 - Bacterially Mediated Oxidation of Ammonium to Nitrite and Nitrate

$$\frac{dN_3}{dt} = \frac{\hat{\mu}_2}{Y_2}\left(\frac{N_2}{K_{s2} + N_2}\right)X_2 \tag{13}$$

$$\frac{dX_1}{dt} = \hat{\mu}_1\left(\frac{N_1}{K_{s1} + N_1}\right)X_1 - K_{d1}X_1 \tag{14}$$

$$\frac{dX_2}{dt} = \hat{\mu}_2\left(\frac{N_2}{K_{s2} + N_2}\right)X_2 - K_{d2}X_2 \tag{15}$$

where X_1 is the concentration of nitrosomonas bacteria, mg/l of dry weight ($105^{o}C$), $\hat{\mu}_1$ is the maximum growth rate of the bacteria, K_{s1} is the half saturation constant, K_{d1} is the bacterial death rate and Y_1 is the yield coefficient. The yield coefficient is defined such that the oxidation of a unit mass of ammonium-nitrogen produces a dry mass Y of bacteria. Corresponding quantities with subscript 2 refer to nitrobacter bacteria. Model 3 has eight rate constants, four for each class of bacteria and five initial values. In general, the initial values for ammonium, nitrite and nitrate are known; however, the initial bacterial concentrations are not usually known and must be regarded as additional data fitting constants. A comparison of Model 3 with the Knowles data is shown in Fig. 7 with values of the constants and initial values given in Table 1:

TABLE 1: Constants and Initial Values for Model 3 in Fig. 7

Nitrosomonas:	$\hat{\mu}_1 = 1.2\ day^{-1}$, $Y_1 = 0.05$, $K_{s1} = 0.6$ mg/l, $K_{d1} = 0.2\ day^{-1}$
Nitrobacter:	$\hat{\mu}_2 = 1.8\ day^{-1}$, $Y_2 = 0.02$, $K_{s2} = 1.7$ mg/l, $K_{d2} = 0.2\ day^{-1}$
Observed initial values:	$N_{10} = 17.5$ mg/l, $N_{20} = N_{30} = 0$
Assumed initial values:	$X_{10} = 0.01$ mg/l, $X_{20} = 0.015$ mg/l

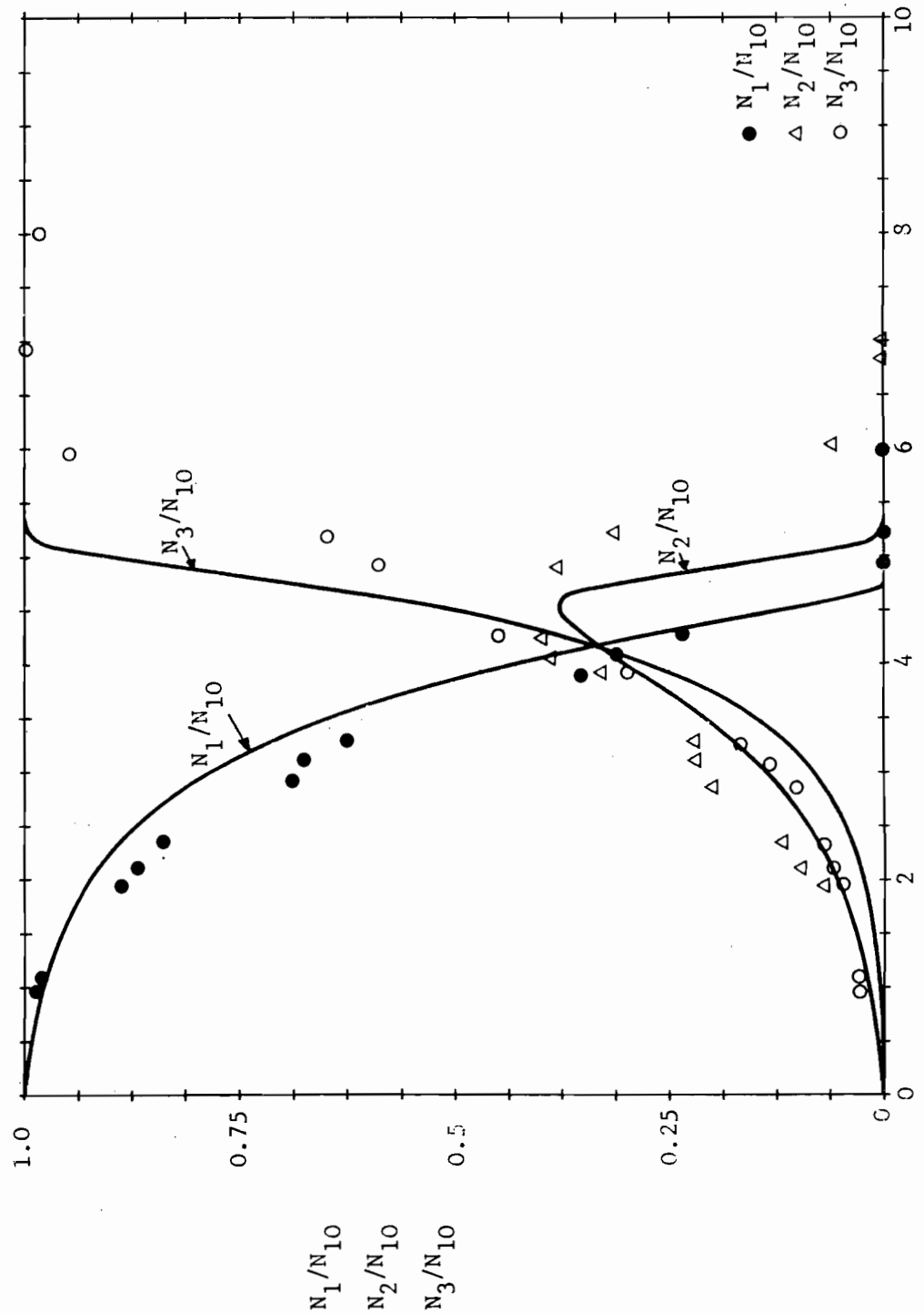

Fig. 7: Comparison of Model 3 with Data of Knowles et al (1965):

Model Constants in Table 1

The solution to equations (11) through (15) for Model 3 were obtained numerically by means of a 4th-order Runge-Kutta scheme. The constants in Table 1 are not necessarily the optimum or "best-fit" values; however, it is evident that Model 3 has the capability of describing the nitrification process in a satisfactory manner. It is also obvious that Model 3, with 10 constants, should provide a better agreement with the data than the previous models containing one and two constants.

At this point, one is faced with the choice of a multi-constant model (No. 3) that describes the dynamics of the nitrification process, or a "simple" model (No. 1 or No. 2) that does not describe the dynamics. If it is accepted that the yield coefficient, Y, the maximum growth rate, $\hat{\mu}$, and the half-saturation constant, K_s, are fundamentally related to the bacterial type, the temperature and the Ph at which the nitrification process occurs, the six constants of Model 3 may be regarded as known within a relatively small range. These values can be obtained from the literature on the growth of nitrifying bacteria or from specific batch or chemostat tests performed on samples of the lake or river water under investigation. Relatively little is known about bacterial death or decay rates, K_d, and they are probably highly variable under specific environmental conditions. Model 3 is relatively insensitive to the decay rates K_{d1} and K_{d2}. This is shown in Fig. 8, where Model 3 is compared to the same data with $K_{d1} = K_{d2} = 0$. An equally good fit of the data is obtained with maximum growth rates reduced to 60% of the former values and new initial values for the nitrifying bacteria. The constants and initial values for Fig. 8 are given in Table 2. The yield coefficients and half-saturation constants are unchanged:

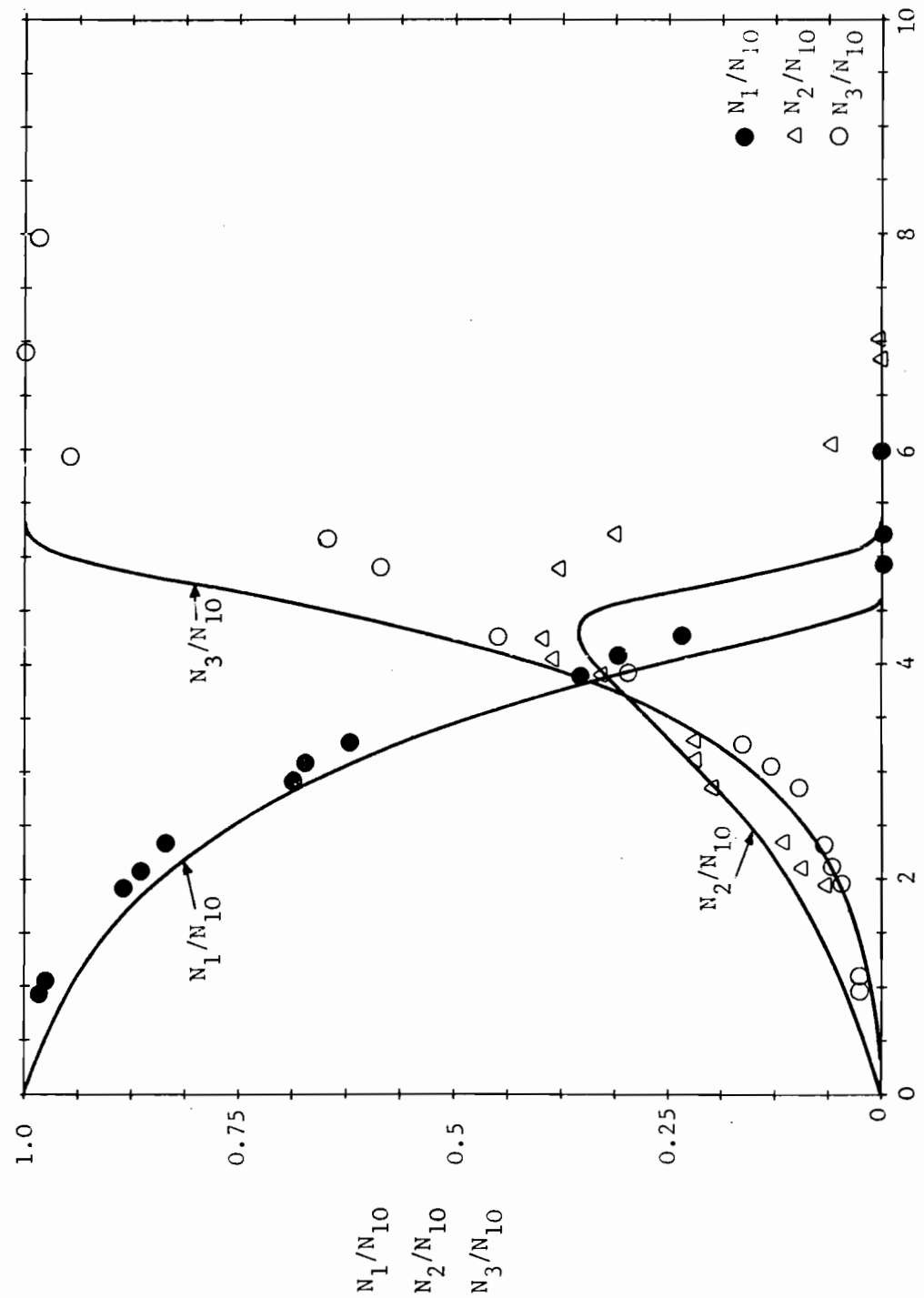

Fig. 8: Comparison of Model 3 with Data of Knowles et al (1965):

Model Constants in Table 2

TABLE 2: Constants and Initial Values for Model 3 in Fig. 8

Nitrosomonas:	$\hat{\mu}_1 = 0.7\ \text{day}^{-1}$, $Y_1 = 0.05$, $K_{s1} = 0.6$ mg/l, $K_{d1} = 0$
Nitrobacter:	$\hat{\mu}_2 = 1.1\ \text{day}^{-1}$, $Y_2 = 0.02$, $K_{s2} = 1.7$ mg/l, $K_{d2} = 0$
Observed initial values:	$N_{10} = 17.5$ mg/l, $N_{20} = N_{30} = 0$
Assumed initial values:	$X_{10} = 0.05$ mg/l, $X_{20} = 0.02$ mg/l

Thus, if the six bacterial constants (Y, $\hat{\mu}$ and K_s) are regarded as "known", Model 3 contains only two data fitting constants, the initial bacterial concentration X_{10} and X_{20}. In this sense Model 3 is comparable with the two constants of Model 2 and is preferable from the standpoint of simulating the dynamics of the nitrification process. Furthermore, the likelihood that first order nitrification rate constants such as K_1 and K_2 in Model 2 are known a priori, or are transferable from one lake or river system to another, is remote.

2.2 Transformation of Organic and Inorganic Nitrogen

A number of additional models, of varying complexity, were considered for all of the non-plankton components of the nitrogen cycle shown in Fig. 1. The simplest model representing the mineralization and subsequent oxidation of particulate and dissolved organic nitrogen, with first order rate constants, is shown in Fig. 9. The equations for the batch system, designated Model 4, are

MODEL 4:
$$\frac{dN_1}{dt} = K_{71}N_7 - K_{12}N_1 \tag{16}$$

$$\frac{dN_2}{dt} = K_{12}N_1 - K_{23}N_2 \tag{17}$$

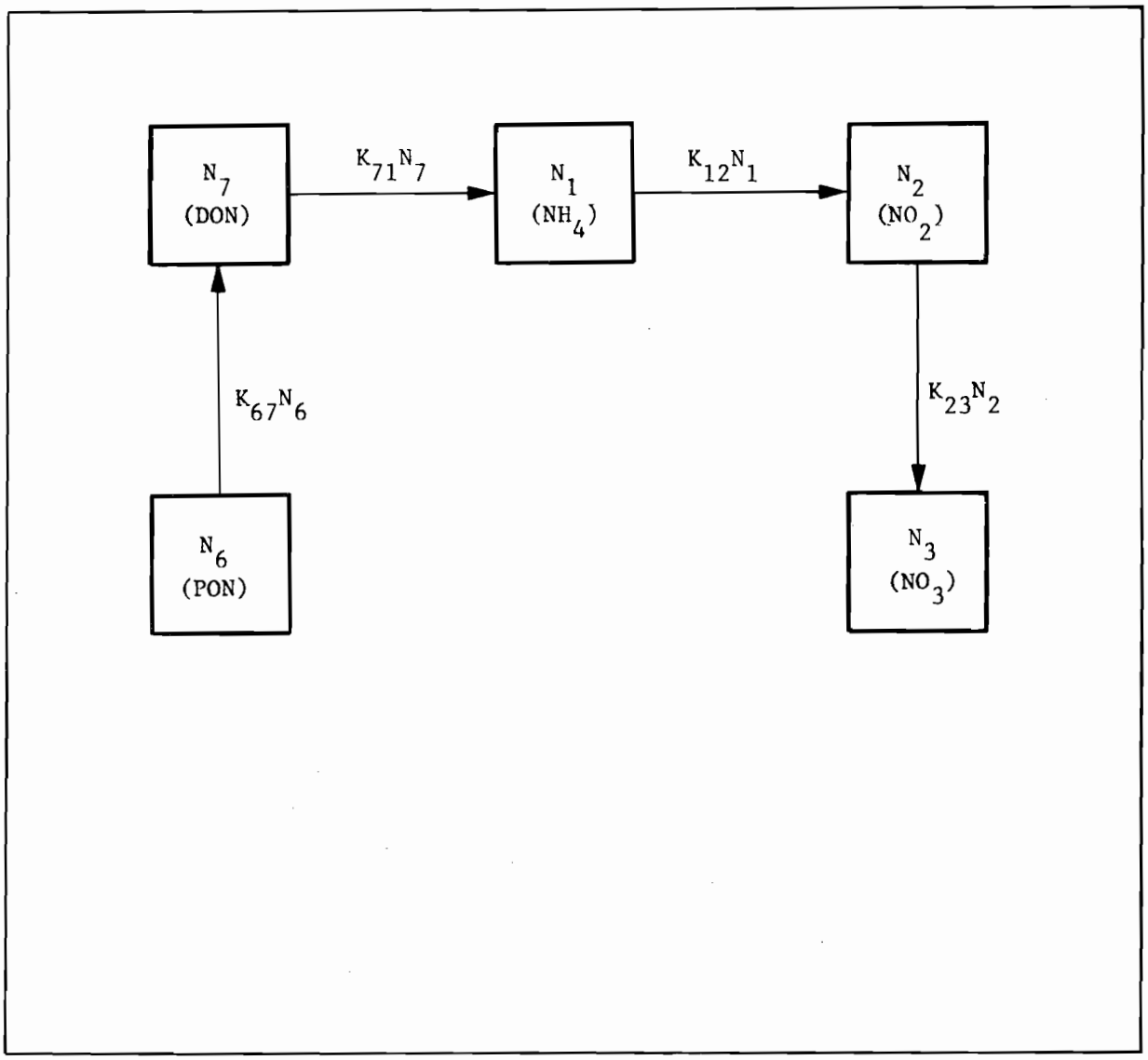

Fig. 9: MODEL 4 - First Order Mineralization and Oxidation of Organic Nitrogen

$$\frac{dN_3}{dt} = K_{23}N_2 \tag{18}$$

$$\frac{dN_6}{dt} = - K_{67}N_6 \tag{19}$$

$$\frac{dN_7}{dt} = K_{67}N_6 - K_{71}N_7 \tag{20}$$

Model 4 has four rate constants and five initial conditions.

Laboratory data (Votintsev, 1948) for a batch system using water from a lake in the USSR having an apparent high initial concentration of dissolved organic nitrogen, is shown in Fig. 10. Unfortunately, nitrogen concentrations were measured only for the inorganic forms. The batch test was conducted under dark conditions at constant temperature (approximately 19°C) for 60 days. The data is interesting in that it shows both the mineralization and nitrification sequences over the period of 60 days, including an unusually high transient production of nitrite in which the maximum concentration of nitrite is essentially equal to the maximum concentration of ammonium. It is well known that the simple first order, consecutive reaction, nitrification model (as represented by Model 2) has a maximum nitrite concentration less than half of the maximum ammonium concentration, as shown in Fig. 5.

The numerical solution of the Model 4 equations (16) through (20) is shown in Fig. 11. The four, first order rate constants given in the caption of Fig. 11, were chosen to simulate the steady-state concentrations at the end of the 60 day test. The initial values for the inorganic components, N_{10}, N_{20} and N_{30} were measured; however, initial values for the particulate and dissolved organic nitrogen N_{60} and N_{70} had to be assumed and are given in the caption of Fig. 11.

As expected, the maximum concentration of nitrite (N_2) is about 50% of the maximum ammonium. For clarity, and because of the lack of agreement of the model

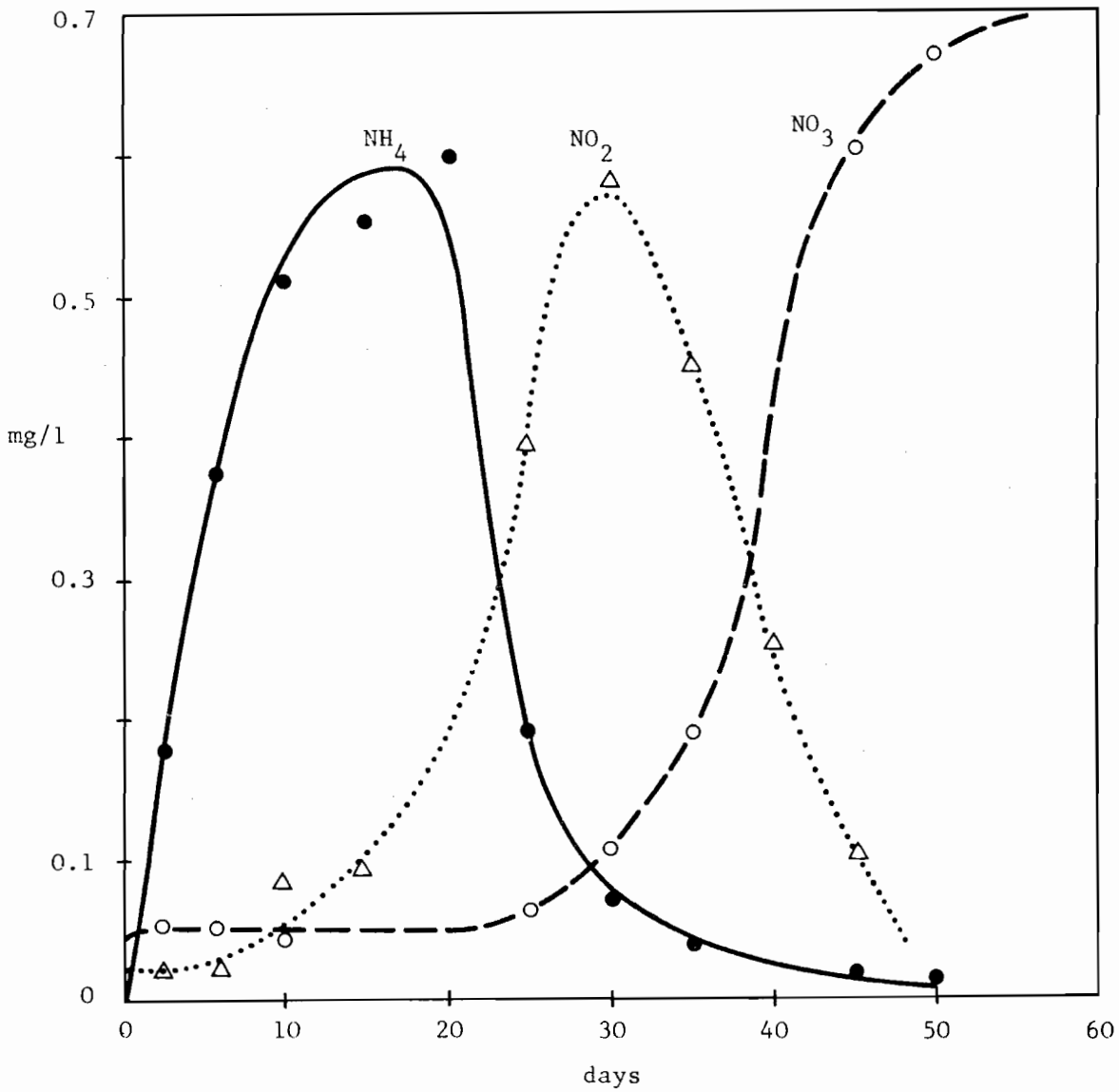

Fig. 10: Batch System Data of Votintsev (1948)

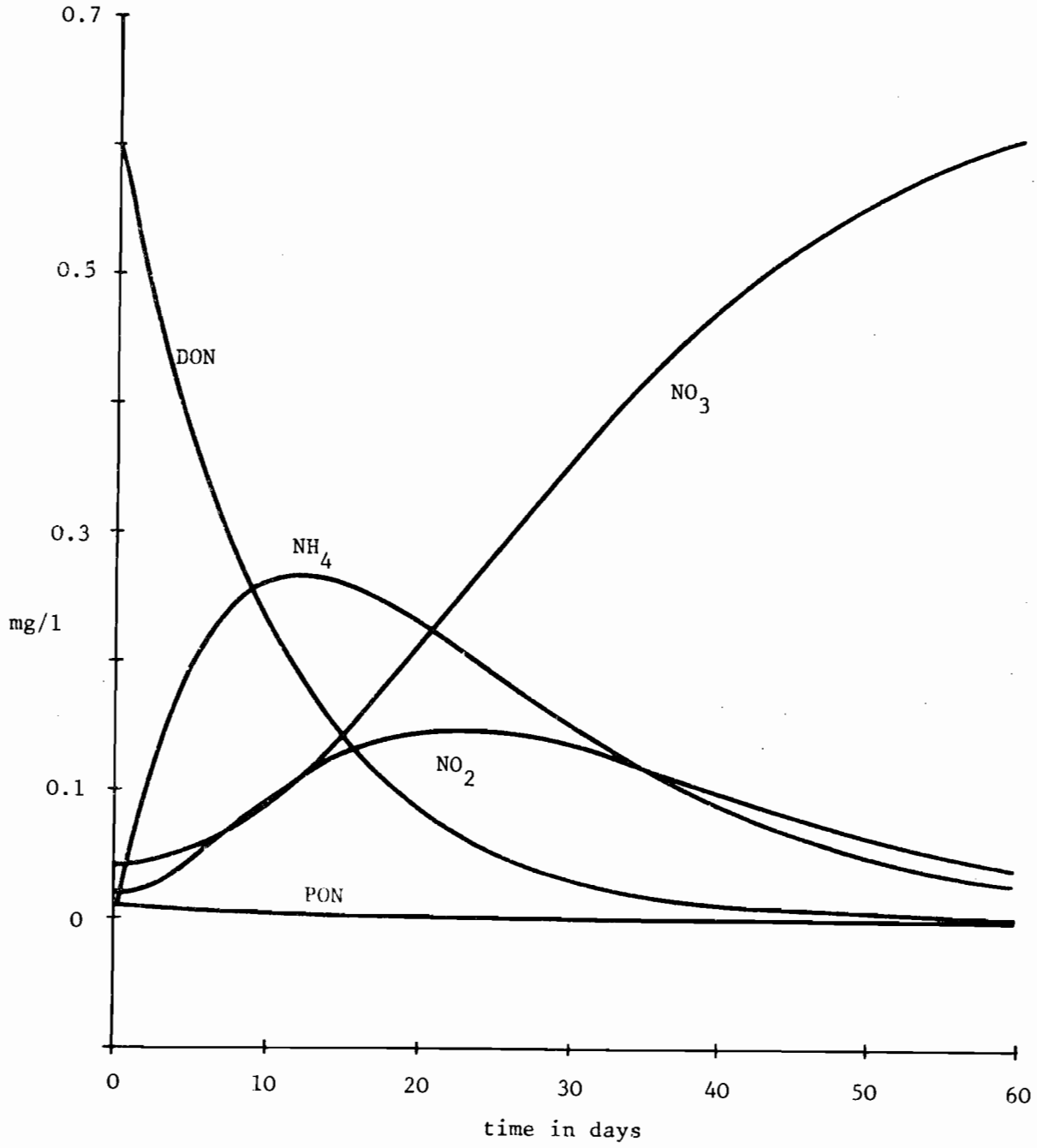

Fig. 11: Results of Model 4 for Comparison with Data of Votintsev (1948):

$K_{12} = 0.07$; $K_{23} = 0.10$; $K_{67} = 0.10$; $K_{71} = 0.10$ (all in day^{-1});

$N_{10} = 0.001$; $N_{20} = 0.02$; $N_{30} = 0.04$; $N_{60} = 0.01$; $N_{70} = 0.6$ (all in mg/1)

and the data, the data has not been superimposed on the model results. However, Figs. 10 and 11 are plotted to the same scale to facilitate comparison.

Following the earlier line of thought on the importance of bacterially mediated processes, the action of heterotrophic bacteria on mineralization or transformation of dissolved organic nitrogen to inorganic nitrogen, is considered in Model 5 as shown diagramatically in Fig. 12. The equations for Model 5 are

MODEL 5:
$$\frac{dN_1}{dt} = -\frac{\hat{\mu}_1}{Y_1}\left(\frac{N_1}{K_{s1} + N_1}\right)X_1 + \frac{\hat{\mu}_7}{Y_7}\left(\frac{N_7}{K_{s7} + N_7}\right)X_7 \tag{21}$$

$$\frac{dN_2}{dt} = \frac{\hat{\mu}_1}{Y_1}\left(\frac{N_1}{K_{s1} + N_1}\right)X_1 - \frac{\hat{\mu}_2}{Y_2}\left(\frac{N_2}{K_{s2} + N_2}\right)X_2 \tag{22}$$

$$\frac{dN_3}{dt} = \frac{\hat{\mu}_2}{Y_2}\left(\frac{N_2}{K_{s2} + N_2}\right)X_2 \tag{23}$$

$$\frac{dN_6}{dt} = -K_{67}N_6 \tag{24}$$

$$\frac{dN_7}{dt} = K_{67}N_6 - \frac{\hat{\mu}_7}{Y_7}\left(\frac{N_7}{K_{s7} + N_7}\right)X_7 \tag{25}$$

$$\frac{dX_1}{dt} = \hat{\mu}_1\left(\frac{N_1}{K_{s1} + N_1}\right)X_1 - K_{d1}X_1 \tag{26}$$

$$\frac{dX_2}{dt} = \hat{\mu}_2\left(\frac{N_2}{K_{s2} + N_2}\right)X_2 - K_{d2}X_2 \tag{27}$$

$$\frac{dX_7}{dt} = \hat{\mu}_7\left(\frac{N_7}{K_{s7} + N_7}\right)X_7 - K_{d7}X_7 \tag{28}$$

where the only new constants are those for heterotrophic bacteria, X_7, and its associated growth, yield and death constants, $\hat{\mu}_7$, K_{s7}, Y_7, K_{d7}.

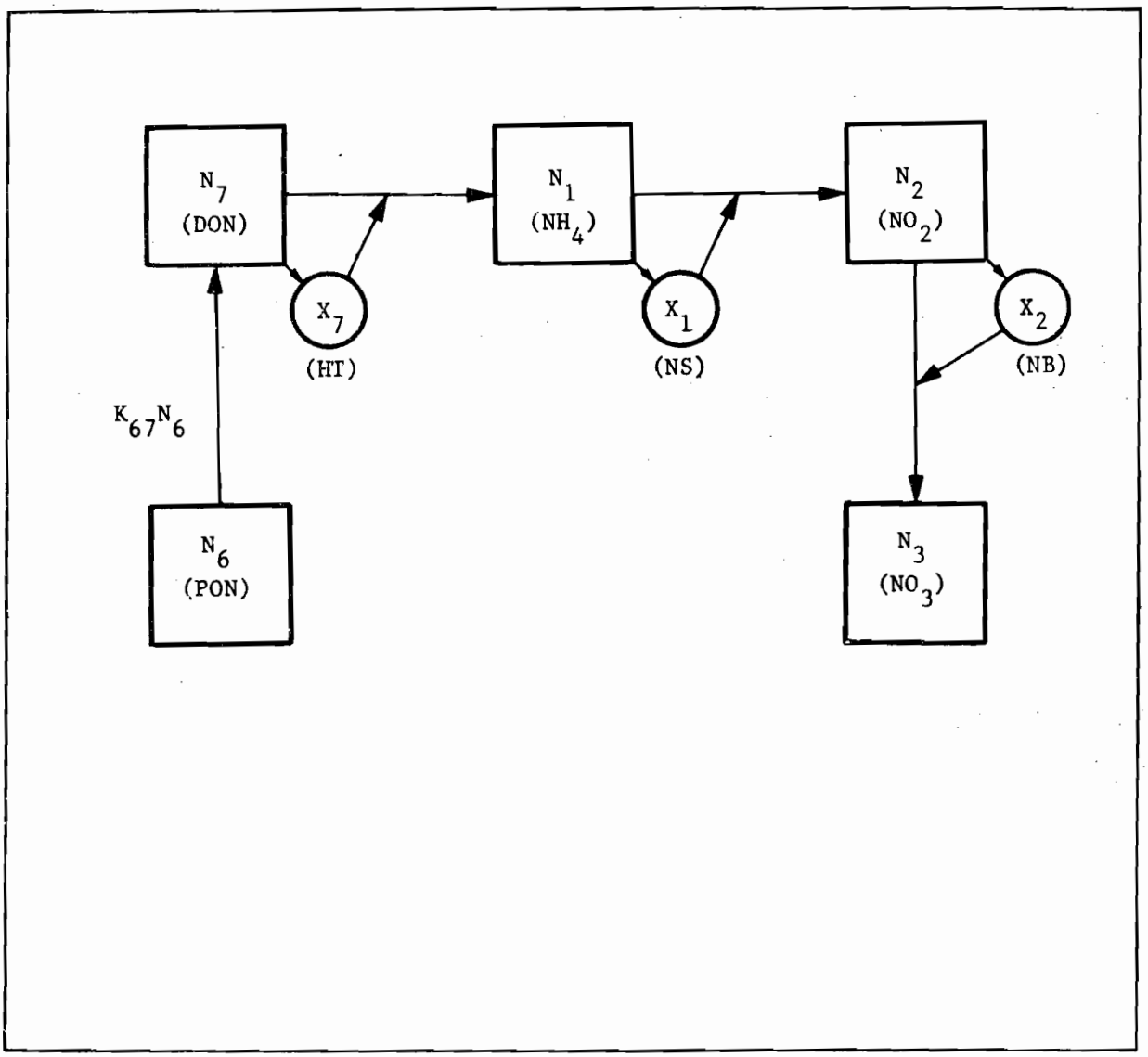

Fig. 12: MODEL 5 - Bacterially Mediated Mineralization and Oxidation of Organic Nitrogen

Model 5 contains a total of 13 constants and requires 8 initial values. However, 8 of the constants, relating to nitrosomonas and nitrobacter, may be assumed equal to those obtained from Model 3 (see Table 1), using the Knowles data.

The numerical solution of the Model 5 equations (21) through (28) is shown in Fig. 13 with constants and initial values given in Table 3.

TABLE 3: Constants and Initial Values for Model 5 in Fig. 13

Nitrosomonas: $\hat{\mu}_1 = 1.2\ day^{-1}$, $Y_1 = 0.05$, $K_{s1} = 0.6$ mg/1, $K_{d1} = 0.2\ day^{-1}$ (Same as Table 1)	
Nitrobacter: $\hat{\mu}_2 = 1.8\ day^{-1}$, $Y_2 = 0.02$, $K_{s2} = 1.7$ mg/1, $K_{d2} = 0.2\ day^{-1}$ (Same as Table 1)	
Heterotrophs: $\hat{\mu}_7 = 1.0\ day^{-1}$, $Y_7 = 0.2$, $K_{s7} = 0.15$ mg/1, $K_{d7} = 0.2\ day^{-1}$	
Particulate Org. N to Dissolved Org. N: $K_{67} = 0.3\ day^{-1}$	
Observed Initial Values (mg/1):	$N_{10} = 10^{-3}$, $N_{20} = 2.10^{-2}$, $N_{30} = 4.10^{-2}$
Assumed Initial Values (mg/1):	$N_{60} = 10^{-2}$, $N_{70} = 0.6$, $X_{10} = 4.10^{-4}$, $X_{20} = 7.10^{-3}$, $X_{70} = 10^{-4}$

The initial values for the five nitrogen parameters N_{10} through N_{70} are the same in Models 4 and 5. The results for Models 4 and 5 (Figs. 11 and 13) are significantly different. With the exception of the first 10 days, Model 5 agrees reasonably well with the Votintsev data. Nearly equal values of maximum ammonium and nitrite concentrations are predicted.

The sensitivity of Model 5 to a change in a bacterial growth constant is shown by comparing Figs. 13 and 14. In Fig. 14, the maximum growth rate for the heterotrophic bacteria was changed from $\hat{\mu}_7 = 1.0$ to $0.5\ day^{-1}$. All other constants and initial values remained the same. This change shifts the

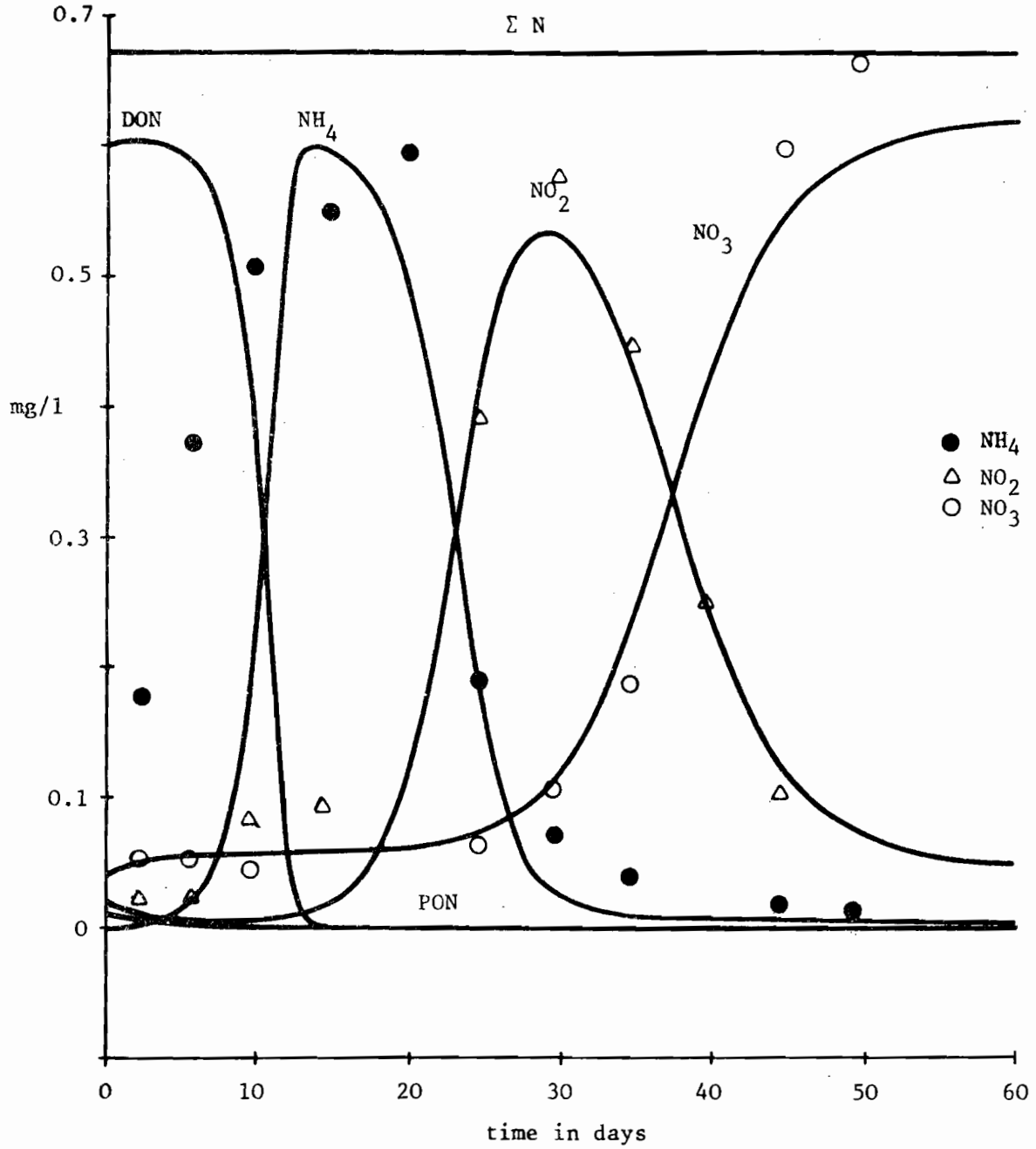

Fig. 13: Comparison of Model 5 with Data of Votintsev (1948):

Model Constants in Table 3

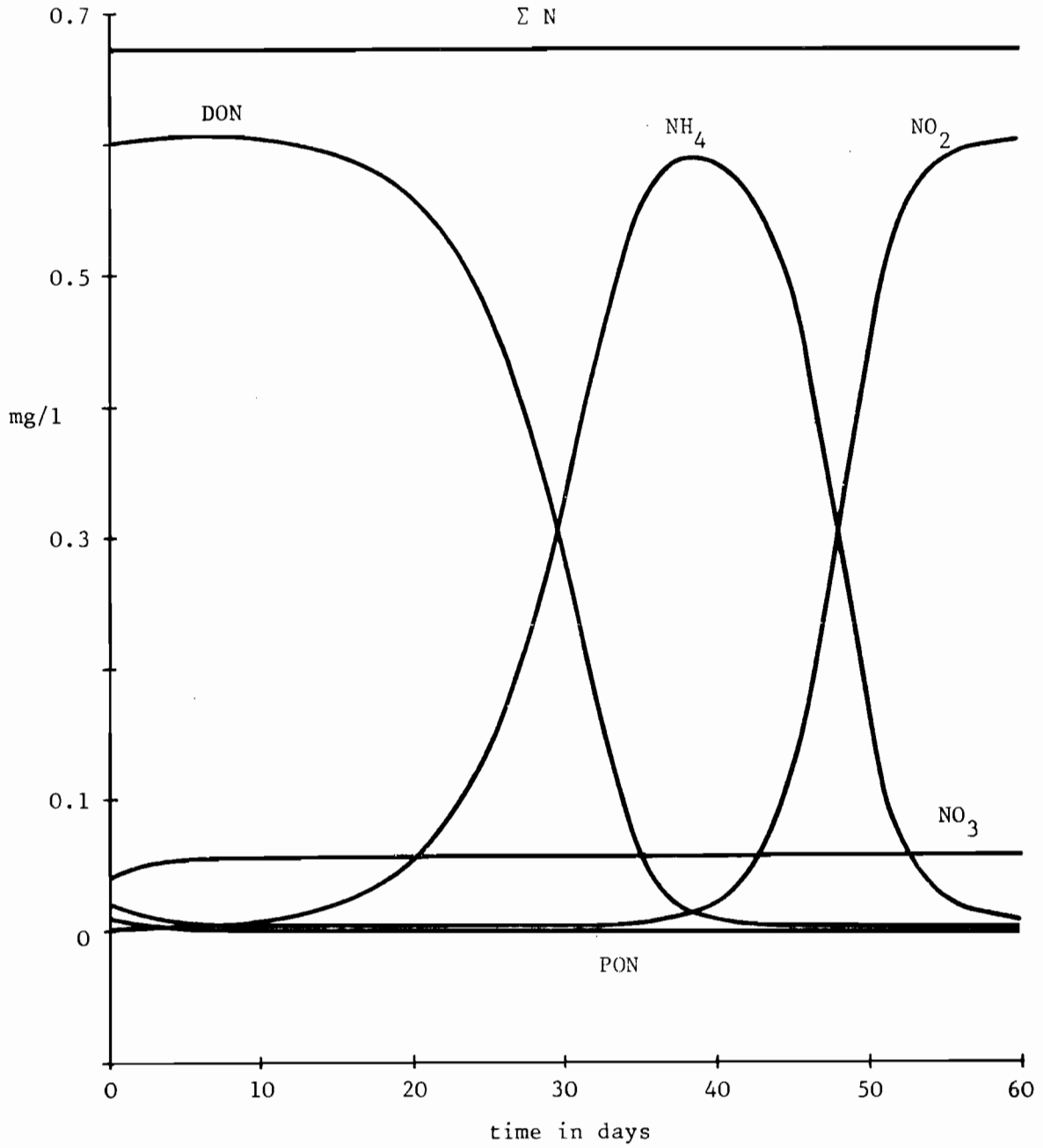

Fig. 14: Sensitivity of Model 5 to change in Heterotrophic Bacterial growth rate. Model Constants in Table 3, except $\hat{\mu}_7 = 0.5\ \text{day}^{-1}$

time of the maximum concentration of ammonium (N_1) from 15 days to 40 days and the increase of nitrate (N_3) is entirely supressed within the 60 day period. The model is also sensitive, but considerably less so, to changes in initial bacterial concentrations. This is shown by comparing Figs. 13 and 15. In Fig. 15, the initial concentration of heterotrophic bacteria was increased by a factor of ten ($X_{70} = 10^{-3}$). Maximum concentrations of ammonium (N_1) and nitrite (N_2) occur 3 to 5 days earlier.

The lack of agreement of Model 5 within the first 10 days may be due to a number of factors not included in the model. For example, the lake water sample used by Votintsev undoubtedly initially contained living phytoplankton. Since the 60 day batch test was conducted under dark conditions, the death rate of the plankton presents an unknown influence on the organic and inorganic nitrogen cycle. In addition, the assumed values for the initial concentrations of particulate (N_6) and dissolved (N_7) organic nitrogen may be incorrect. The Votintsev data has been used by Leonov (1975) in the modelling of bacterially mediated processes. He also used additional batch system data for sewage water and seawater. Recently Leonov (1978) has developed at IIASA more sophisticated ecological models, including bacterial growth inhibition due to the formation of metabolic products. This model offers another possible explanation for the initial 10 day period.

Model 5, as well as the previous models considered in this study, are structured to conserve the element nitrogen as identified by the appropriate components shown in Fig. 1. In the models containing additional bacterial components, the nitrogen content of the bacteria is not included in the total mass conservation of nitrogen. Justification for this simplification can be provided by considering Fig. 16, which shows the calculated bacterial concentrations for Model 5, using the constants and initial values of Table 3. The maximum dry weight concentration of the heterotrophic bacteria is 0.075 mg/l.

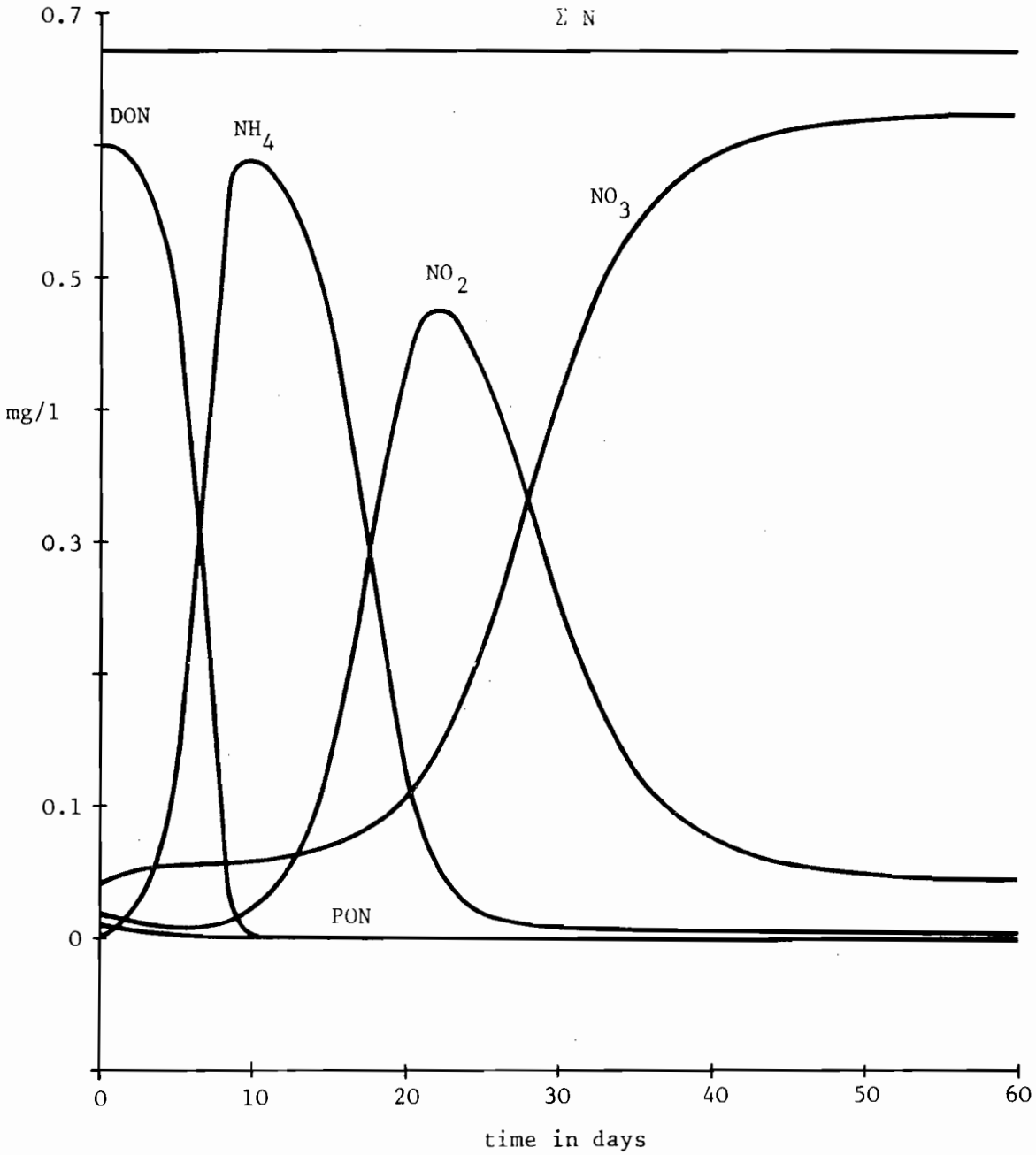

Fig. 15: Sensitivity of Model 5 to change in Initial Concentration of Heterotrophic Bacteria. Model Constants in Table 3, except $X_{70} = 10^{-3}$ mg/l

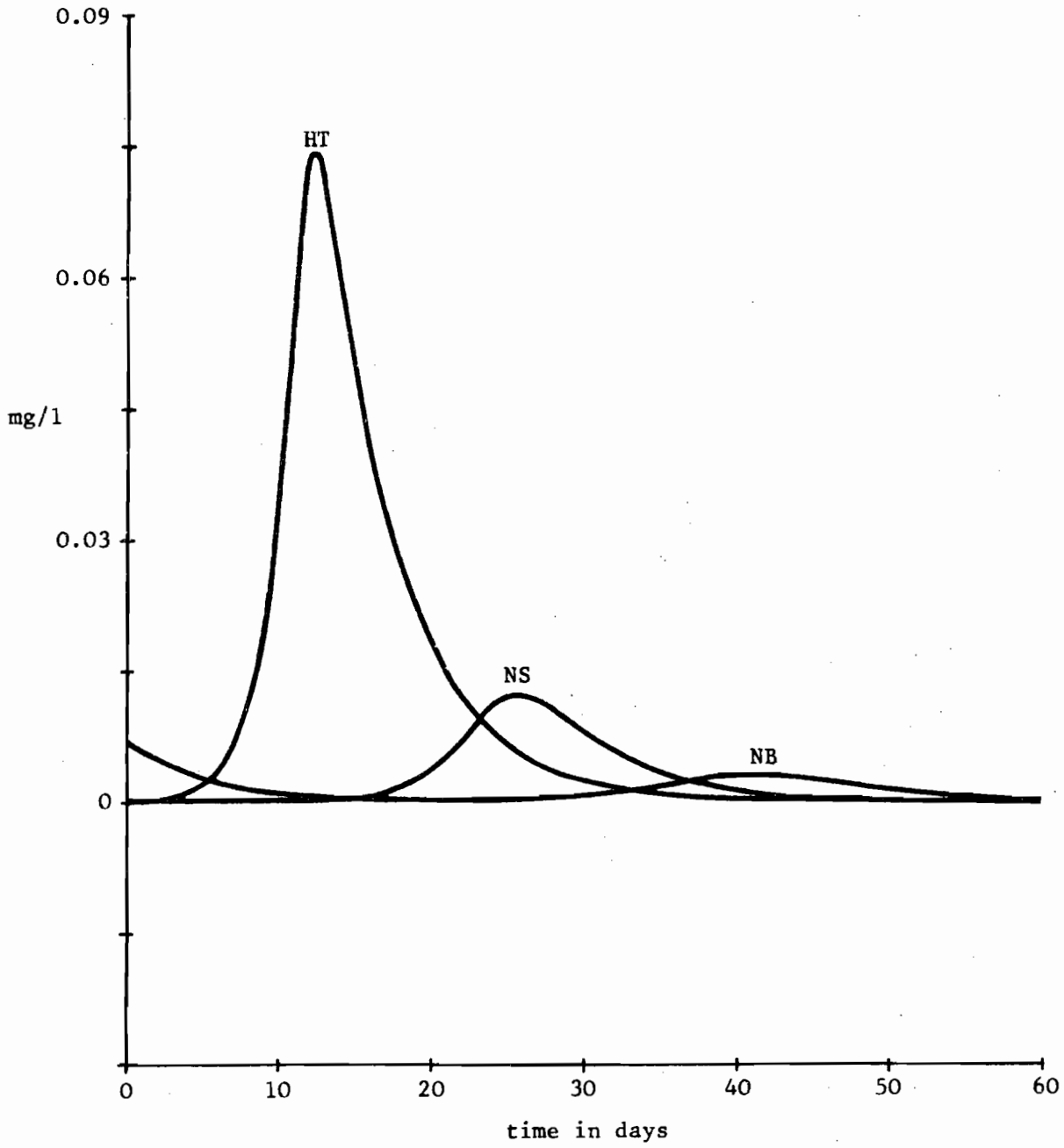

Fig. 16: Bacteria Concentrations, Model 5, Constants in Table 3

Assuming the nitrogen content at 10% of dry weight, the maximum bacterial contribution is of the order of 1% of the total nitrogen concentration. The horizontal line labelled ΣN in Figs. 13, 14 and 15 shows that the calculated $\Sigma N = N_1 + N_2 + N_3 + N_6 + N_7$ is constant.

The use of the same bacterial rate constants for comparing the different data sets of Models 3 and 5 demonstrates the concept of transferability of basic transformation process information between physical systems. It should be mentioned that both the Knowles et al (1965) and Votintsev (1948) batch tests were conducted at similar temperatures ($19^{o}C$). Therefore, it was not necessary to consider the temperature dependance of bacterial growth rates and saturation constants.

An argument frequently used in favor of linear, first order reactions, as opposed to Michaelis-Menten kinetics, is that the two are equivalent when the concentration of the substrate is small compared to the half-saturation constant. This argument does not apply to the bacterially mediated reactions of Models 3 and 5. For example, if $N_1 << K_{s1}$ and $K_{s1} + N_1 \simeq K_{s1}$, equations (11) and (14) can be written as,

$$\frac{dN_1}{dt} = - (\frac{\hat{\mu}_1}{Y_1 K_{s1}}) N_1 X_1 \tag{29}$$

$$\frac{dX_1}{dt} = (\frac{\hat{\mu}_1}{K_{s1}}) N_1 X_1 - K_{d1} X_1 \tag{30}$$

The decrease of N_1 with time remains coupled to the time varying bacterial growth rate, thus equation (29) is not equivalent to a first order reaction as in equation (5).

2.3 Closure of the Nitrogen Cycle with Plankton

In this section models for all of the aerobic nitrogen components shown in Fig. 1, including phyto- and zooplankton, are considered. In contrast to the open end models 1 through 5, Model 6 , shown diagramatically in Fig. 17, simulates

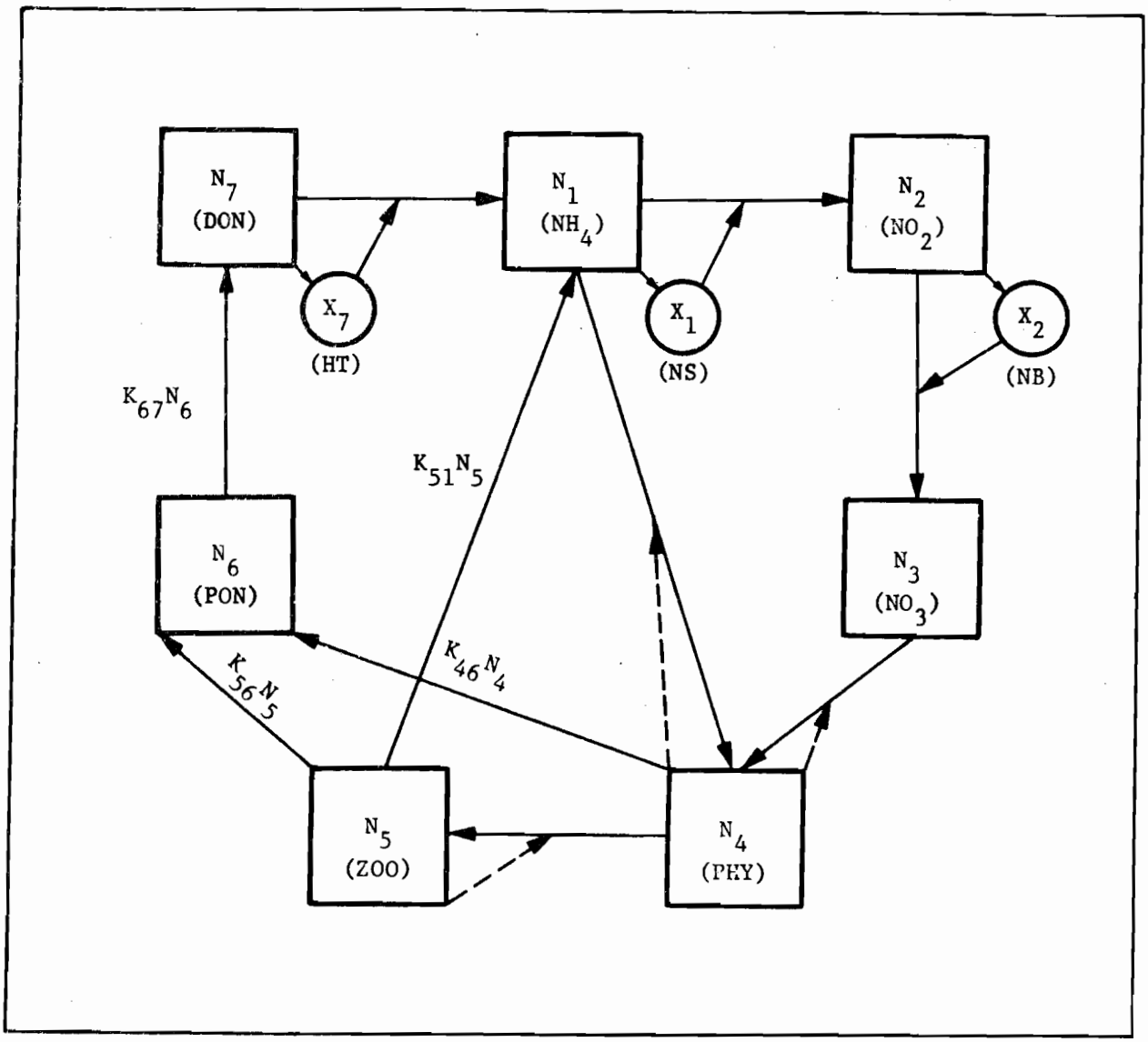

Fig. 17: MODEL 6 - Closed Nitrogen Cycle--Bacterially Mediated Mineralization and Oxidation with Plankton (---- indicates Michaelis-Menten Kinetics for Phytoplankton Uptake and Zooplankton Grazing)

a closed nitrogen cycle. Model 6 incorporates the total Model 5 sub-cycle, i.e. the first order transformation from particulate organic nitrogen (N_6) to dissolved organic nitrogen (N_7) and the bacterially mediated transformations to ammonium (N_1), nitrite (N_2) and nitrate (N_3). Michaelis-Menten kinetics are assumed for separate expressions for the uptake of nitrate and ammonium by phytoplankton (N_4) and the grazing of zooplankton (N_5) on phytoplankton. Constants not previously defined are the maximum phytoplankton uptake rates and saturation constants for ammonium ($\hat{\mu}_{14}$, K_{s14}), nitrate ($\hat{\mu}_{34}$, K_{s34}) and the zooplankton grazing rates ($\hat{\mu}_{45}$, K_{s45}). Inhibition by ammonium of nitrate uptake by phytoplankton has been observed by a number of investigators [see Conway (1974)]. Although not included here, the expression for maximum uptake rate $\hat{\mu}_{34}$ could be modified to account for this effect [see Najarian and Harleman (1975)]. Ammonium regeneration by phytoplankton, as well as the temperature and light dependance of phytoplankton uptake rates and zooplankton grazing rates, are omitted, as these effects are not pertinent to the model comparisons.

Three additional first order reactions complete the plankton portions of the closed nitrogen cycle: ammonium regeneration by zooplankton (K_{51}), formation of particulate organic nitrogen by death and defecation of zooplankton (K_{56}) and death of phytoplankton (K_{46}). Lysis and leakage from phytoplankton directly to dissolved organic nitrogen is assumed to be negligible in comparison to the other nitrogen transformation processes.

The Model 6 equations for a batch system are,

$$\underline{\text{MODEL 6:}}\quad \frac{dN_1}{dt} = -\frac{\hat{\mu}_1}{Y_1}\left(\frac{N_1}{K_{s1} + N_1}\right)X_1 + \frac{\hat{\mu}_7}{Y_7}\left(\frac{N_7}{K_{s7} + N_7}\right)X_7 + K_{51}N_5 - \hat{\mu}_{14}\left(\frac{N_1}{K_{s14} + N_1}\right)N_4 \tag{31}$$

$$\frac{dN_2}{dt} = \frac{\hat{\mu}_1}{Y_1}\left(\frac{N_1}{K_{s1} + N_1}\right)X_1 - \frac{\hat{\mu}_2}{Y_2}\left(\frac{N_2}{K_{s2} + N_2}\right)X_2 \tag{32}$$

$$\frac{dN_3}{dt} = \frac{\hat{\mu}_2}{Y_2}\left(\frac{N_2}{K_{s2} + N_2}\right)X_2 - \hat{\mu}_{34}\left(\frac{N_3}{K_{s34} + N_3}\right)N_4 \tag{33}$$

$$\frac{dN_4}{dt} = \hat{\mu}_{14}\left(\frac{N_1}{K_{s14} + N_1}\right)N_4 + \hat{\mu}_{34}\left(\frac{N_3}{K_{s34} + N_3}\right)N_4 - \hat{\mu}_{45}\left(\frac{N_4}{K_{s45} + N_4}\right)N_5 - K_{46}N_4 \tag{34}$$

$$\frac{dN_5}{dt} = \hat{\mu}_{45}\left(\frac{N_4}{K_{s45} + N_4}\right)N_5 - K_{51}N_5 - K_{56}N_5 \tag{35}$$

$$\frac{dN_6}{dt} = K_{46}N_4 + K_{56}N_5 - K_{67}N_6 \tag{36}$$

$$\frac{dN_7}{dt} = K_{67}N_6 - \frac{\hat{\mu}_7}{Y_7}\left(\frac{N_7}{K_{s7} + N_7}\right)X_7 \tag{37}$$

$$\frac{dX_1}{dt} = \hat{\mu}_1\left(\frac{N_1}{K_{s1} + N_1}\right)X_1 - K_{d1}X_1 \tag{38}$$

$$\frac{dX_2}{dt} = \hat{\mu}_2\left(\frac{N_2}{K_{s2} + N_2}\right)X_2 - K_{d2}X_2 \tag{39}$$

$$\frac{dX_7}{dt} = \hat{\mu}_7\left(\frac{N_7}{K_{s7} + N_7}\right)X_7 - K_{d7}X_7 \tag{40}$$

Model 6 contains a total of 22 constants and requires ten initial concentrations for the seven nitrogen components and the three types of bacteria. A simulation run, shown in Fig. 18, based on a numerical solution of the Model 6 equations (31) through (40), was made using the rate constants for nitrosomonas, nitrobacter and heterotrophic bacteria obtained in the previous examples. The additional rate constants for the phytoplankton and zooplankton cycling were obtained from the literature and are summarized in Table 4. References to a number of literature sources for rate constants for bacterial and algal components of the nitrogen cycle are given in the concluding section.

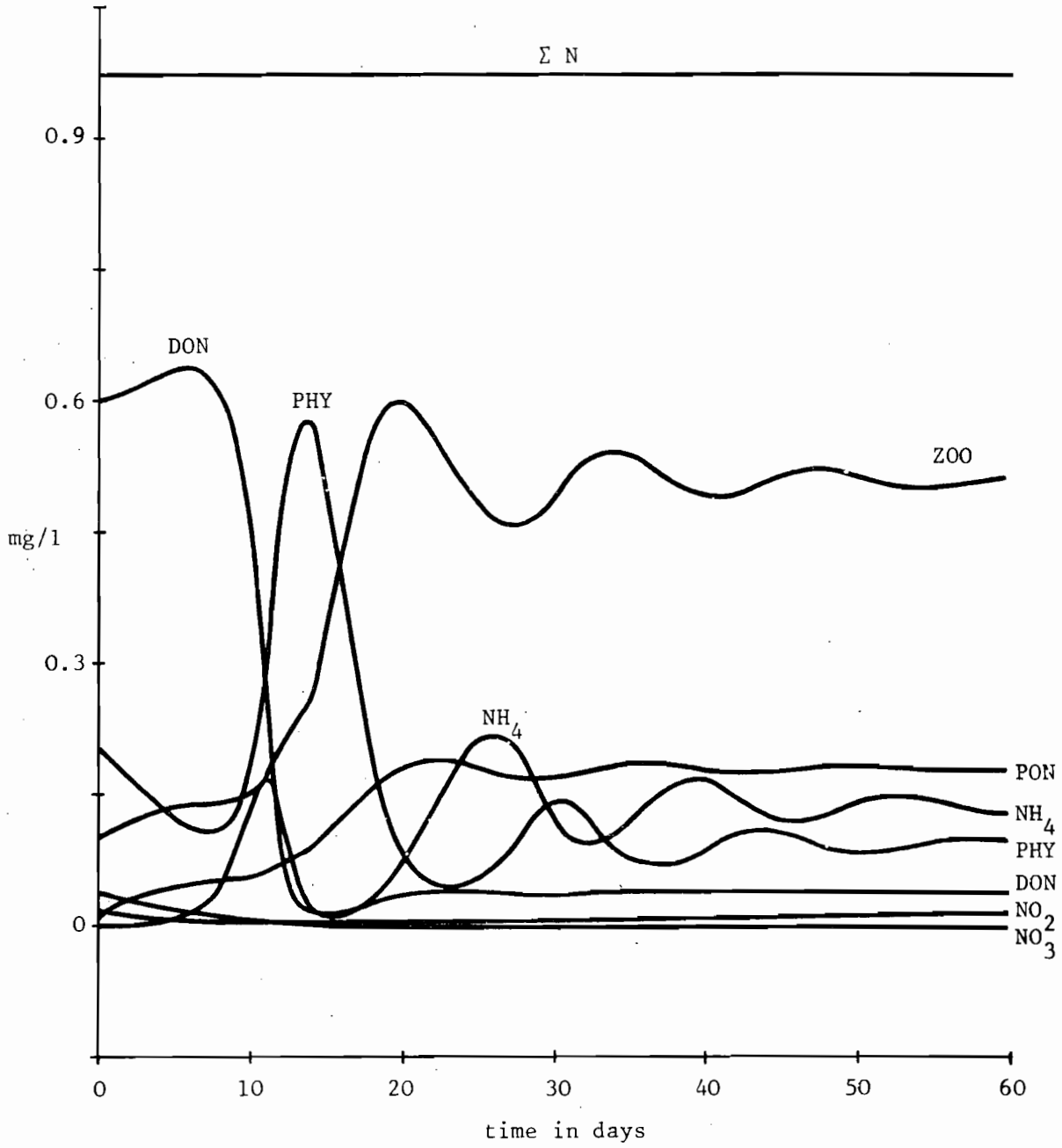

Fig. 18: MODEL 6 - Closed Cycle Simulation Run.

Model Constants in Table 4

TABLE 4: Constants and Initial Values for Model 6 in Fig. 18

All constants and initial values given in Table 3 for Model 5 are used in Model 6. Additional constants and initial values required for Model 6 are as follows:

Uptake of NH_4 by Phytoplankton:	$\hat{\mu}_{14} = 2.0\ day^{-1}$, $K_{s14} = 0.3$ mg/l
Uptake of NO_3 by Phytoplankton:	$\hat{\mu}_{34} = 1.0\ day^{-1}$, $K_{s34} = 0.7$ mg/l
Zooplankton grazing:	$\hat{\mu}_{45} = 0.7\ day^{-1}$, $K_{s45} = 0.5$ mg/l
Phytoplankton death rate:	$K_{46} = 0.03\ day^{-1}$
NH_4 regeneration by zooplankton:	$K_{51} = 0.01\ day^{-1}$
Death and defecation of zooplankton:	$K_{56} = 0.1\ day^{-1}$
Assumed initial values:	$N_{40} = 0.2$ mg/l, $N_{50} = 0.1$ mg/l

A comparison of Figs. 13 (Model 5) and Fig. 18 (Model 6) shows the effect of plankton cycling on the redistribution of the nitrogen components starting with the same initial values. Unfortunately, no data sources involving plankton were available for comparison with the Model 6 batch system simulations.

Model 7 was constructed to investigate the importance of the bacterially mediated Michaelis-Menten reactions for the transformation of dissolved organic and inorganic nitrogen relative to the Michaelis-Menten reactions for phytoplankton uptake and zooplankton grazing. Model 7, shown in the diagram of Fig. 19, is a combination of the linear, first order reactions for dissolved organic and inorganic nitrogen of Model 4, with the Michaelis-Menten phyto- and zooplankton interactions of Model 6. The complete set of nitrogen cycle equations for Model 7 are,

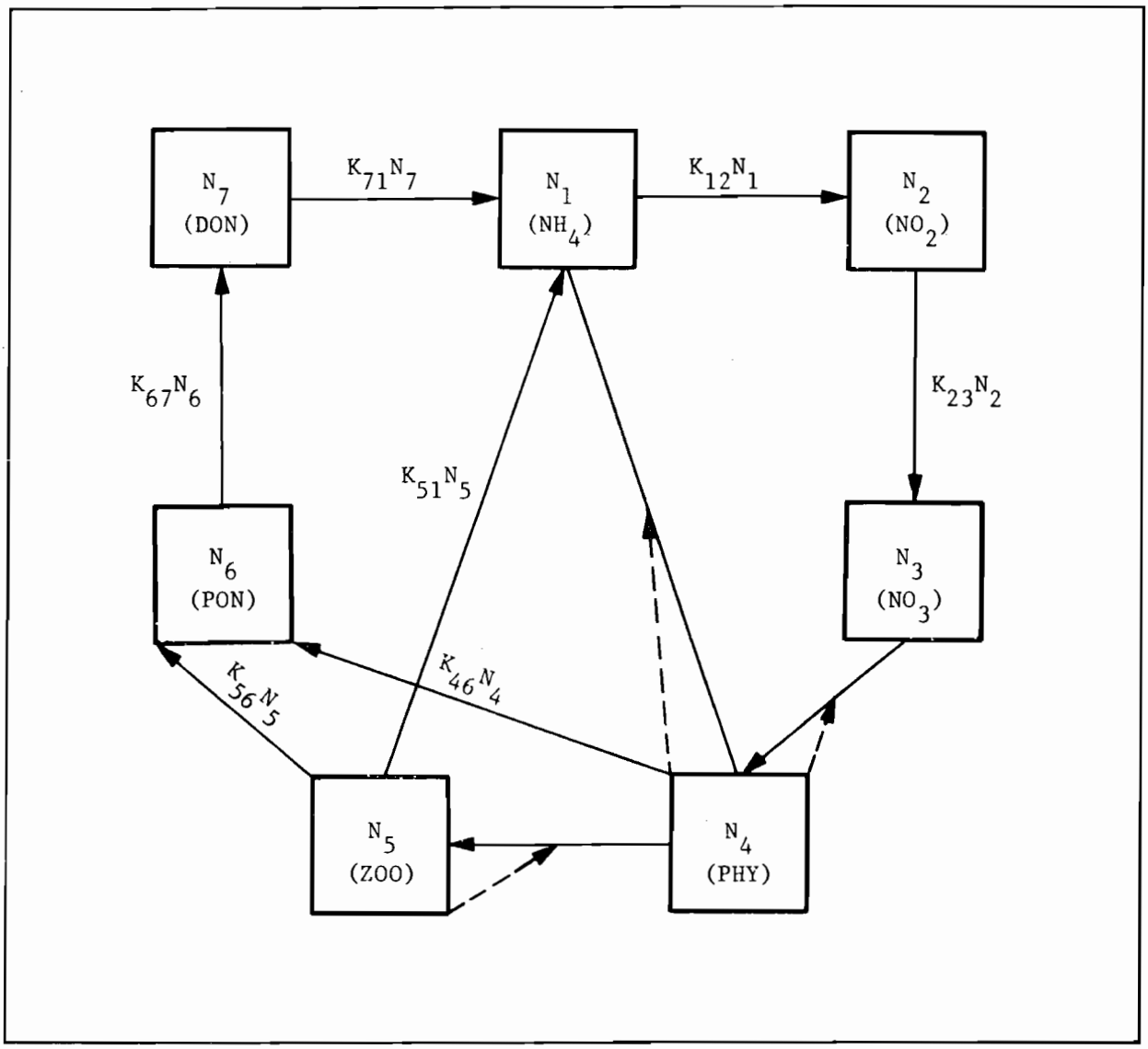

Fig. 19: MODEL 7 - Closed Nitrogen Cycle--First Order Mineralization and Oxidation with Plankton (---- indicates Michaelis-Menten Kinetics for Phytoplankton Uptake and Zooplankton Grazing)

MODEL 7:

$$\frac{dN_1}{dt} = - K_{12}N_1 + K_{71}N_7 + K_{51}N_5 - \hat{\mu}_{14}\left(\frac{N_1}{K_{s14} + N_1}\right)N_4 \quad (41)$$

$$\frac{dN_2}{dt} = K_{12}N_1 - K_{23}N_2 \quad (42)$$

$$\frac{dN_3}{dt} = K_{23}N_2 - \hat{\mu}_{34}\left(\frac{N_3}{K_{s34} + N_3}\right)N_4 \quad (43)$$

$$\frac{dN_4}{dt} = \hat{\mu}_{14}\left(\frac{N_1}{K_{s14} + N_1}\right)N_4 + \hat{\mu}_{34}\left(\frac{N_3}{K_{s34} + N_3}\right)N_4 - \hat{\mu}_{45}\left(\frac{N_4}{K_{s45} + N_4}\right)N_5 - K_{46}N_4 \quad (44)$$

$$\frac{dN_5}{dt} = \hat{\mu}_{45}\left(\frac{N_4}{K_{s45} + N_4}\right)N_5 - K_{51}N_5 - K_{56}N_5 \quad (45)$$

$$\frac{dN_6}{dt} = K_{46}N_4 + K_{56}N_5 - K_{67}N_6 \quad (46)$$

$$\frac{dN_7}{dt} = K_{67}N_6 - K_{71}N_7 \quad (47)$$

Model 7 contains 13 constants and requires seven initial values for the seven nitrogen storage variables. The four constants for the first order organic-inorganic transformation used in the Model 7 simulation, shown in Fig. 20, are the same as those used in Model 4 (see caption in Fig. 11). The phyto- and zooplankton constants are the same as used in Model 6 and the initial values for the nitrogen variables are common to all three models (see Table 4).

Comparison of Figs. 11 (Model 4) and 20 (Model 7) shows the effect of plankton in closing the nitrogen cycle, where first order kinetics are assumed for the organic-inorganic transformations. More importantly, Figs. 18 and 20 for the two closed-loop nitrogen cycles, show the influence of bacterially mediated, organic-inorganic transformations in Model 6, in comparison with the first order reactions in Model 7. In the Model 6 simulation (Fig. 18) 50 to 60 days are required to reach steady state conditions, whereas in the Model 7 simulation (Fig. 20), steady

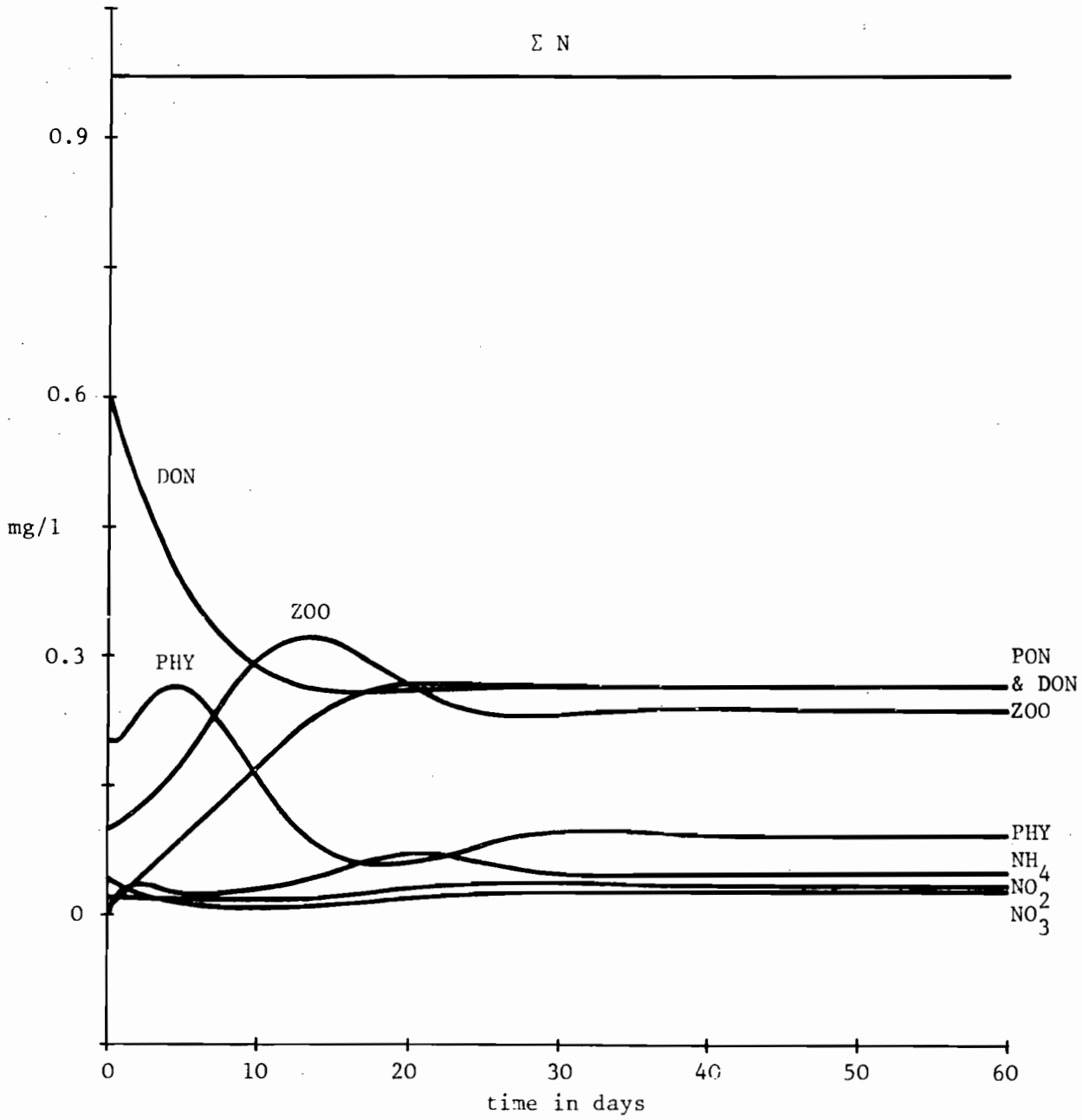

Fig. 20: MODEL 7 - Closed Cycle Simulation Run.

Model Constants in Caption of

Fig. 11 and Table 4

state is reached in 30 days. In addition, the predicted steady state concentrations of the seven nitrogen state variables are completely different in the two models. For example, the ratio of zooplankton to phytoplankton nitrogen in Model 6 is 4.7; in Model 7 it is 2.4; the rate of dissolved organic nitrogen to phytoplankton in Model 6 is 0.4 and in Model 7 it is 2.6.

3. Summary and Conclusions

For the nitrification sub-cycle, Models 1 and 2 with first order rate constants were compared with Model 3, which described the bacterially mediated oxidation processes. Model 3 agrees with batch data, whereas Models 1 and 2 do not. The constants in Model 3 are attributed to Michaelis-Menten constants for the oxidizing bacteria, nitrosomonas and nitrobacter.

Models 4 and 5 extended the modelling effort to include the particulate and dissolved forms of non-living organic nitrogen as well as the nitrification sequence. Model 4 contained first order rate constants throughout, while Model 5 included the non-linear processes of Model 3, plus a third bacterial process for converting dissolved organic matter to ammonium. Models 4 and 5 were compared with batch data from another source. There was a general lack of agreement of the first order rate processes of Model 4 in relation to Model 5. Model 5 utilized the two sets of oxidizing bacterial rate constants of Model 3 and attributed the additional set of Michaelis-Menten constants to heterotrophic bacteria.

The nitrogen cycle of Fig. 1 was closed by the addition of phytoplankton and zooplankton nitrogen components in Models 6 and 7. Both models assumed Michaelis-Menten kinetics for uprate of nutrients by phytoplankton and zooplankton grazing. Model 6 included the bacterially mediated mineralization-oxidation processes, while Model 7 assumed these to be first order. Batch system simulation runs with Models 6 and 7 were made. From a comparison of the results it is concluded that the non-linear, bacterially mediated, mineralization and oxidation reactions exert a strong influence on both the dynamics and steady

state of the full nitrogen cycle.

Justification for the additional complexity and number of constants required for the models containing bacterial components as opposed to the "simpler" first order models requires additional discussion. From a numerical computational standpoint, the differences are insignificant. It is always true that the ability to match data increases as the number of model constants increases. Therefore, justification for more complex models, such as those including bacterial processes, must be made on the basis that these constants tend to have a more fundamental or universal nature than those of the simpler first order models. This has important implications on the ability to transfer rate process information from one physical system to another and in predicting the response of a single system to changes in inputs.

The strength of the transferability argument depends upon the degree to which biochemical processes can be isolated and identified. Within the past decade progress in the qualitative and quantitative understanding of element cycling has been rapid. A number of references, primarily concerned with the nitrogen cycle, contain a significant amount of information on non-linear rate processes for the models considered in this study. General review articles on the aquatic nitrogen cycle include those by Keeney (1972), Wuhrmann and Gujer (1976), and Sharma and Ahlert (1977). Other more specific references to the modelling of bacterial processes in the mineralization and oxidation of nitrogen compounds include Painter (1970), Nihoul (1975), Steele (1975), Mortimer (1975) and Golterman (1975).

4. Future Research

Additional comperative studies on both single and combined element cycle water quality models, particularly as they apply to lakes and reservoirs, are needed. For the most part models developed by individuals have been used on a specific lake. Rarely are different models compared to the same set of data.

A first step in this direction would be to investigate models of the type discussed in this study for continuous stirred tank reactors (CSTR). The batch system models can be converted to CSTR's by the addition inflow and outflow terms, in which case they are applicable to fully mixed lakes. Further comparative studies should be made on the modelling of sediment interactions, on discrete layer models and on models that describe a continuous, vertical distribution of water quality parameters. Recent progress in modelling advection and mixing processes, as observed in density and temperature distributions, in deep lakes, opens a fruitful field for comparative studies of combined hydrophysical and ecological models. The interaction of the total nitrogen cycle model with the complex hydrodynamics and mixing processes in an estuary has been demonstrated by Najarian and Harleman (1975).

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Computer Programs for the Mathematical Models

A total of seven mathematical models were used in this study. Model 1 has an analytical solution, equations (3) and (4). Models 2 and 4 can be run as special cases of Model 7. Models 3 and 5 can be run as special cases of Model 6.

A User's Manual has been prepared for Models 6 and 7 (designated as programs H-6 and H-7 in IIASA's program file) and is available as a separate IIASA Research Memorandum by Serge Medow.