

Working Paper

THE CHEMICAL-ECOLOGICAL MODELING
OF AQUATIC NITROGEN COMPOUND
TRANSFORMATION PROCESSES

Alexandre Leonov

May 1980
WP-80-86

**International Institute for Applied Systems Analysis
A-2361 Laxenburg, Austria**

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PREFACE

This report deals with an ecological problem of water quality studies, namely the biogeochemical cycles of nutrient compounds and the mechanisms of their transformation in water. Study results presented here are a contribution within the framework of Task 2 "Environmental Quality Control and Management", and especially of Subtask 2A "Hydrophysical and Ecological Models for Water Quality" in IIASA's Resources and Environment Area.

The paper contains two complex ecological models for studying the biochemical cycles of nitrogen and oxygen.

This study was conducted between September 1977 - April 1978. The overall purpose of the study was the examination of ecological models in order to determine the possibility of applying these models to reproduce experimental observations of nitrogen transformations in various water environments. Such observations are the basis for identification of rate constants used in mathematical models of water quality.

ACKNOWLEDGEMENTS

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I am specially grateful to Larissa Mazour who devoted her skills and time in translating this paper from Russian into English. I would also like to thank Serge Medow (Canada) who made computer programs for running the models at IIASA's Computer Center.

ABSTRACT

Nitrogen compounds are important biogeochemical substances that influence the state of water quality. Since transformation of nitrogen compounds is carried out in various water environments (sewage, river, sea and lake waters), it is important to know the rates of these processes. Mathematical models were used for this purpose.

Models for nitrogen compound transformation, including both very simple, purely chemical models and complex ecological models, have already been studied at IIASA (RM-78-34). In this report results from the application of other complex ecological models are presented.

The models are constructed using the principles of biogeocoenosis modeling. The primary objective of this paper is to make a comparative study of the simulation capabilities of different nitrogen transformation models using a given set of experimental data. Modeling results of nitrogen transformation are compared with experimental observations of sewage, river, sea and lake waters. Nitrogen transformations are interpreted from the ecological point of view and are defined by interactions between different microorganisms (bacteria, phytoplankton and zooplankton) and nitrogen compounds (organic and mineral). Two ecological models are presented in this report. It is shown that models constructed on the basis of biochemical compound transformations have broader simulation capabilities than simple models. The model presented here shows good agreement between observed and predicted nitrogen compound concentrations. The model also provides an explanation of the effects of nitrogen transformations on the oxygen content in water environments. However, at present the models discussed cannot be considered entirely adequate for the ecological processes which they

describe, although they reproduce in detail the nitrogen transformations in various waters. The absence of multi-aspect experimental observations, specifically carried out for determining the boundaries of model adequacy, impedes the development of applied research on water quality modeling.

The complex ecological models discussed in this report can be used for understanding processes of nitrogen transformations in different water environments. At the same time, these models can also be applied for constructing models of combined biogeochemical cycles of carbon, phosphorus and oxygen, and for simulating functions of aquatic ecosystems as well as for studying various aspects of water quality.

CONTENTS

1.	INTRODUCTION	1
2.	MODELING CONCEPTS	12
3.	DESCRIPTION OF MODEL NO. 1	14
3.1	Plankton Community	16
3.1.1	<i>Uptake of Nutrients by Plankton Organisms</i>	17
3.1.2	<i>Plankton Excretions</i>	28
3.1.3	<i>Plankton Mortality</i>	30
3.2	Detritus	30
3.3	Nitrogen Compounds	31
3.4	Oxygen	33
4.	SIMULATION RUNS AND DISCUSSION	38
5.	DESCRIPTION OF MODEL 2	52
6.	SIMULATION	67
6.1	Simulation of Nitrogen Transformation in Sewage and River Waters	67
6.2	Simulation of Nitrogen Transformation in Sea and Lake Waters	78
7.	GENERAL DISCUSSION OF SIMULATION RESULTS	88
8.	SUMMARY AND CONCLUSIONS	109
9.	PROSPECTS FOR FUTURE RESEARCH AT IIASA	111
	REFERENCES	113

THE CHEMICAL-ECOLOGICAL MODELING
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TRANSFORMATION PROCESSES

A. Leonov

1. INTRODUCTION

Until quite recently studies on water quality and self-purification of water bodies used only general integral characteristics for describing the state of water quality. The state variables most frequently used for describing these processes were the content of dissolved oxygen and biochemical oxygen demand (BOD). The Streeter-Phelps model suggested in 1925 has found exceptionally wide application. This is due to the fact that this model describes the oxygen regime balance and its dependence on labile organic matter content (in units of BOD). However, nowadays the use of this model cannot always be justified. The integral characteristics are less informative because of the increasingly complex composition of the pollutants. Thus, these variables are not sufficient for solving ecological problems that occur with changes in the scale and nature of the pollution.

The main aim of current research is to analyze biogeochemical cycles of elements that comprise the composition of living matter and the so-called biophylic, biogenic or organogenic elements (Kovda, 1975). In this respect the most interesting studies that can be carried out are those for the carbon, nitrogen, phosphorus,

sulphur and oxygen cycles, which can be done either separately or in combination with each other. The different compounds of these elements are also a substantial part of the pollutant components of the biosphere and thus determine the water body status and the quality of natural waters.

Experimental studies on the kinetics of biophysical element transformations have been conducted independently of each other. There exists scattered information on the study of separate elements and the links of their common cycles; there have also been studies on some problems of kinetics and transformation mechanisms of these elements' compounds, including their chemical, biochemical and biological features. There are considerable difficulties in estimating correctly the transformation rates of biogenic element compounds both in natural and laboratory conditions owing to the diverse spread of information. It is mainly due to this fact that it is so difficult to reveal any interdependence between the chemical structure of the matter, kinetics and mechanisms of their transformation in water ecological systems (Pitter 1976).

Presently there are three almost unrelated classical trends in the study of element transformation:

- (i) kinetics of decreasing concentrations of chemical compounds;
- (ii) kinetics of utilization, and research on biochemical conversion of substrates by microorganisms; and
- (iii) mechanisms converting individual compounds and their classification, including the determination of rates and the degree of completeness of the transformation processes.

Attempts have been made to generalize the data on these questions by means of mathematical modeling. In connection with this research, there is also a need for developing mathematical models of chemical matter transformation in order to predict the state of a water body for water quality management purposes. Moreover, the problems of both the protection and rational use of water resources, and the problems of modeling the broad biogeochemical

condition of water bodies that are exposed to pollution are particularly relevant.

Nitrogen compounds are some of the most important bio-geochemical substances that affect the biological productivity of natural waters. The main nitrogen forms in natural waters that are generally known are:

- dissolved molecular nitrogen (N_2);
- numerous organic nitrogen compounds, including the products of decomposition from complex proteins to simple amino-acids;
- ammonium (in the form of NH_3 and ammonium ions NH_4^+);
- nitrite (in the form of nitrite ions NO_2^-);
- nitrate (in the form of nitrate ions NO_3^-).

These nitrogenous compounds can enter the hydrosphere along with all kinds of anthropogenic pollution products; they can also enter by natural means, mainly through fixation of atmospheric nitrogen. The physical, photochemical and bacterial mechanisms of atmospheric nitrogen fixation may be subdivided (Hutchinson, 1957). The bacterial fixation of molecular nitrogen is accomplished most readily. The biochemical process of molecular nitrogen fixation, assimilation of its separate forms by microorganisms, and denitrification determine the content of nitrogen compounds in water.

In the process of biological transformation, nitrogen undergoes a complicated cycle of consecutive conversions, the results of which are bound to microorganism biomass, then dispersed and redistributed in the form of organic and mineral components that comprise the chemical composition of the water (Botan et al, 1960).

Different microorganisms (bacteria, algae and plants) assimilate the organic nitrogen compounds of ammonium, nitrite and nitrate in order to meet their demand for nitrogen. Ammonium nitrogen is one of the products of organic matter decomposition by heterotrophic bacteria. The nitrite is formed mainly by bacterial oxidation of ammonium and by nitrate reduction. The final product of the nitrogen transformation--the nitrate--is

formed mainly by the oxidation of ammonium and nitrite by microorganisms. Some parts of the nitrite-nitrogen enters the natural water via atmospheric precipitation and surface flow (Hutchinson, 1957).

The nitrogen bound in the biomass and assimilated in the form of organic and inorganic compounds consists of protein compositions and other biochemically important components of the microorganism cells. During the organisms' life and decay organic and mineral nitrogen compounds are released.

Microorganisms consume nitrogen under a broad spectrum of environmental conditions. In some cases this process is accompanied by changes of the valent state of the nitrogen, but this does not always happen. The valent state of nitrogen in water media changes in different compounds from -3 to +5 (Goering, 1972). Nitrate-nitrogen as a final product of mineralization can be used in anaerobic conditions as an oxygen source and energetic substrate for biosynthetic reactions (Painter, 1970).

Since transformations of the nitrogen compound occur in different water environments (fresh and sea water, sewage, etc.) it is important to know the rates of these processes, and the feasibility of their control and management. This is especially necessary for studying the eutrophication of natural water and the impact of different nitrogen compounds on the behaviour of a natural ecological water system. Natural water quality is to a great extent determined by the content of organic and mineral nitrogen compounds. The high content of organic nitrogen causes the formation of anaerobic conditions, especially near the interface of the sediment and water. The increase of mineral nitrogen compounds promotes the eutrophication of water bodies (Nikolaev, 1975), i.e. excessive acceleration of bioproductive processes by enriching water with biogenic matter. In some cases the intensification of eutrophication is determined by the industrial and domestic discharges of wastewaters, and in other cases by a change in thermal regime caused by thermal discharges which accelerate the turnover and mobilization of biogenic elements, especially in the upper euphotic layer.

Theoretical questions of nitrogen compound transformations caused by microorganisms have already been studied sufficiently. Considerable empirical data on the research of nitrogen compounds in natural water and their transformation rates have been accumulated. There are thorough reviews which have contributed much to research in the field of microbiological transformation of nitrogen compounds in water (Alexander, 1965; Goering, 1972; Golterman, 1960; Painter, 1970; Ruban, 1961; Sharma, Ahlert, 1977). The results of these studies are partially generalized in a number of detailed surveys devoted to nitrification problems and the elucidation of the role of nitrogen in the functions of water ecological systems (Curtis et al, 1975; Goering, 1972; Keeney, 1972; Leonov, Ajzatullin, 1977; Martin, Goff, 1973; Sharma, Ahlert, 1977). However, the available publications do not consider the mechanisms and kinetics of nitrogen compound transformation that have already been studied (Curtis et al, 1975; Round, 1965). This fact considerably limits the possibilities for broad application of the experimental data for optimization of the processes of sewage treatment, for prediction of self-purification rates of natural water, and for problems of water quality research (Leonov, Ajzatullin, 1977).

The main reason for the complexity of this research lies in the fact that practically all types of microorganisms (autotrophs, heterotrophs, chemoautotrophs) take part in the conversion processes of nitrogen compounds. The content of the mineral nitrogen matter depends mainly on the transformation rates of organic nitrogenous compounds by the heterotrophic bacteria. The transformation products of some organisms are used as a food source and energetic substrate for other organisms. For instance, the reduced product of heterotrophic metabolism (ammonium) takes part in the turnover of the chemoautotrophic bacteria species *Nitrosomonas*.

Thus the concentration changes of nitrogen compounds in natural water are a result of the following simultaneous biochemical processes:

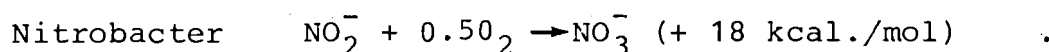
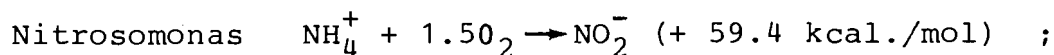
- accumulation, excretion and uptake of the organic nitrogen components by heterotrophic microorganisms and water plants;
- the fermentative hydrolytic destruction of proteins and polypeptides in solution and as particulates;
- the biological transformation of organic particulate nitrogen and living matter nitrogen;
- the formation of ammonium at the de-amination processes of dissolved and cellular organic matter;
- the oxidation of ammonium, nitrite, and intermediate products by autotrophic nitrifying organisms;
- the assimilation of ammonium, nitrite and nitrate by autotrophic as well as heterotrophic bacteria;
- the reduction of nitrite and nitrate by denitrifying organisms, especially in bottom sediments;
- the fixation of atmospheric nitrogen by water plants and bacteria;

(Alexander, 1965; Botan et al, 1960; Curtis et al, 1975; Goering, 1972; Golterman, 1960; Ierusalimsky, 1963; Keeney, 1972; Leonov, Ajzatullin, 1977; Martin, Goff, 1975; Painter, 1970; Sharma, Ahlert, 1977).

Knowledge of the rates of all chain and separate transformation stages of nitrogenous matter obtained from experimental laboratory studies is fragmentary. Generally, the range of the rates of only two processes have been sufficiently studied: consumption and regeneration of nitrogen compounds by algae with respect to primary productivity; and nitrification, in connection with water quality problems (Leonov, Ajzatullin, 1977).

In a water ecosystem the oxidative transformation of a number of intermediate nitrogenous products--hydroxylamine, dihydroxyammonium, nitroxyl, hyponitrite--is relatively fast (Ruban, 1961). For example in natural water hydroxylamine, a first product of ammonium transformation (Alexander, 1965), is oxidized at 25°C in 2-3 hours (Fiadeiro et al, 1967). Oxidation of ammonium and nitrite occur slowly. These reactions limit the

general rates of the nitrogen compound transformations. Two populations of chemautotrophic bacteria fulfil the oxidation of ammonium and nitrite:



These two stages are taken into account while modeling the nitrogen cycle in water. It has been suggested that the oxidation of ammonium and nitrite occurs by fermentation, each respective fermentation being closely connected with the cell structures of the chemoautotrophic bacteria where these bacteria are present in small quantities in the solution (Ruban, 1961).

The principal approach to modeling the transformation of separate nitrogen compounds is generalized in the review by Leonov and Ajzatullin (1977). The very first models of nitrogen compound transformations included separate and unconnected simple reactions of first order, such as are used for describing organic nitrogen oxidation to ammonium (the ammonification stage) or ammonium oxidation to nitrate (the nitrification stage) (Maksimova, 1972; Skopintsev, 1938; Skopintsev, Brook, 1940). Mathematical modeling of the utilization of mineral nitrogenous sources by phytoplankton and nitrifying bacteria employs Michaelis-Menten and Monod kinetic expressions. The applicability of these models in solving water quality problems is rather limited and therefore the results obtained from calculations for any sort of prediction should be regarded with caution unless adequate bounds for such simple models are established (Leonov, Ajzatullin, 1977).

Recently, due to the development of systems studies, more complicated mathematical models have been used for the research of nitrogen compound transformations. Some of the schemes for modeling nitrogen compound transformations are shown in Table 1. Schemes 1-3 describe the transformation of nitrogen compounds as a sequence of first-order reactions (Ajzatullin, 1967; Anderson et al, 1976; Bronfman, Iljchev, 1976; Miyake, Wada, 1968). They

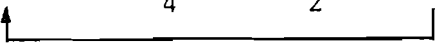
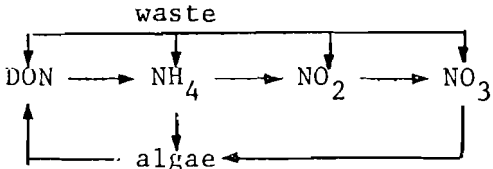
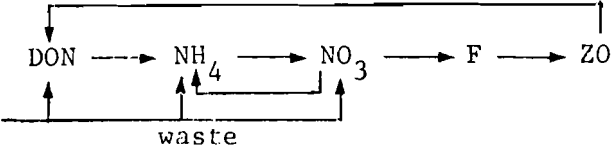
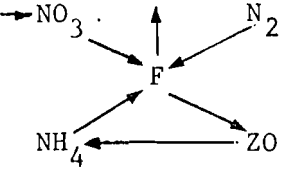
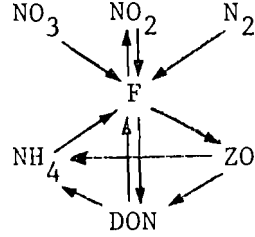
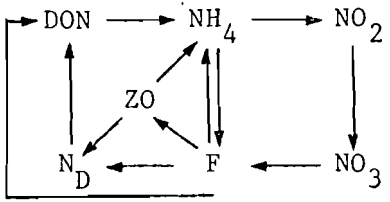
differ only in the number of components taken into account. Simple transformation models of nitrogen compounds presented in the form of first order chemical equations (Maksimova, 1972; Skopintsev, 1938; Skopintsev, Brook, 1940), as well as equations for sequential conversion of nitrogen compounds (Ajzatullin, 1967; Anderson et al, 1976; Bronfman, Iljchev, 1976; Miyake, Wada, 1968), have been based on purely chemical considerations. However, these simplified models cannot cover all the experiments on nitrogen compound transformations. Microorganisms which utilize organic and mineral nitrogen compounds have a significant influence on the kinetics of nitrogen compound transformations. Heterotrophic bacteria consume organic nitrogen compounds while autotrophic bacteria consume mineral compounds.

In all the above-mentioned models it is presumed that the concentrations of bacteria responsible for nitrogen compound transformation are invariable and their biomasses are included in the values of rate constants. However, the concentrations of microorganisms that oxidize, for example, ammonium and nitrite may change in the processes of bacterial development by 2-3 orders of magnitude (DeMarco et al, 1967, Miyake, Wada, 1968). It is essential that the conversion activity of microorganisms is variable.

Mathematical models which take into account bacterial growth (schemes 9, 10, 11) (Ajzatullin, Leonov, 1975a, b; Leonov, Ajzatullin, 1975a, b) are capable of presenting a detailed picture of the dynamics of nitrogen compound transformations as observed in different waters (lake, sea water and sewage).

Ecological balance models (Dugdale, 1967; Lebedev, 1967) describe the turnover of nitrogen only in a general way and are therefore not considered in this report. The ecological models that take into account the interaction of phytoplankton and zooplankton on mineral nitrogenous matter conversions (schemes 4/Penumalli et al, 1976; 5/Ikeda, Adachi, 1976; 6/Dugdale, Goering, 1967; 7/Goering, 1972; 8/Najararian, Harleman, 1975 in Table 1) describe nitrogen compound transformations in a comparatively simple fashion. This is also true for models that cover a more

Table 1. Some Schemes used for mathematical modeling of nitrogen transformations

NN	SCHEMES	REFERENCES
1	$\text{DON} \longrightarrow \text{NH}_4 \longrightarrow \text{NO}_2 \longrightarrow \text{NO}_3$	Ajzatullin, 1967; Mijake, Wada, 1968
2	$\text{N}_D \longrightarrow \text{DON} \longrightarrow \text{NH}_4 \longrightarrow \text{NO}_2 \longrightarrow \text{NO}_3$	Bronfman, Iljchev, 1976
3	$\text{DON} \longrightarrow \text{NH}_4 \longrightarrow \text{NO}_2 \longrightarrow \text{NO}_3$ 	Anderson et al, 1976
4		Penumalli et al, 1976
5		Ikeda, Adachi, 1976
6		Dugdale, Goering, 1967
7		Goering, 1972
8		Najarian, Harleman, 1975

(contd.)

Table 1 (contd.)

NN	SCHEMES	REFERENCES
9		Ajzatullin, Leonov, 1975a; Leonov, Ajzatullin, 1975b
10		Leonov, Ajzatullin, 1975a,b
11		Ajzatullin, Leonov, 1975b; Leonov, Ajzatullin, 1975b
12		Goering, 1972
13		Thomann et al, 1974

Note: DON = dissolved organic nitrogen; NH₄ = ammonium; NO₂ = nitrite; NO₃ = nitrate; N_D = detritus; F = phytoplankton; O₂-deficit = oxygen deficit; BOD = biochemical oxygen demand.

diverse composition of media components (schemes 12/Goering, 1972; and 13/Thomann et al, 1974). These models have been applied in studying eutrophication and process of water quality formation. The simulation capabilities of such models is increased when the influence of temperature and light intensity on the activity of phytoplankton is included. However, for studying the dynamics of a water ecological system it is important that the chemical and biological elements responsible for the nitrogen compound conversions are included in the relevant models. Hence the problems of describing the kinetics of the various stages of microbiological oxidation and transformation of nitrogen compounds should be solved at a chemical-ecological level. It is also necessary to take into consideration the various interactions between the main nitrogen compounds and populations of microorganisms.

Since some attempts at modeling the microbiological nitrogen compound transformations (Ajzatullin, Leonov, 1975a, b; Leonov, Ajzatullin, 1975a, b) and primary productivity processes (Dugdale, Goering, 1967; Goering, 1972; Najarian, Harleman, 1975; Thomann et al, 1974) have already been made, it is obviously interesting to combine these two independent trends.

At the International Institute for Applied Systems Analysis (IIASA) in the "Resources and Environment Area" research on several different problems of water resources protection are being conducted. This includes the studies on the ecological consequences of increasing pollutant discharges, on eutrophication, on self-purification processes, and so forth. Under the direct supervision of Prof. O.F. Vasiliev, who is the Corresponding Member of the USSR Academy of Sciences, the Leader of the Resources and Environment Area, and the Deputy Director of IIASA, research on modeling the biogeochemical nitrogen cycle has been conducted at IIASA between September 1977 and March 1978. Mathematical models for the nitrogen compound transformation, including both the most simple, purely chemical models, and ecological models for the different microorganisms, have been studied by Harleman (1978). He used kinetic expressions of the Michaelis-Menten and Monod type for describing the microorganism dynamics. In this paper ecological models constructed according

to the principles of biogeocoenosis modeling (Poletaev, 1968), with modified Michaelis-Menten and Monod kinetics, are presented. These models were developed from the synthesis of a large amount of information about microorganism behavior in order to explain and to explore a number of hypotheses about nitrogen transformations. This paper presents the results of the examination of models with modified expressions for describing the uptake of nutrients by planktonic organisms. Results of model comparisons with experimental observations on the nitrogen transformations in different water environments are discussed.

2. MODELING CONCEPTS

Current knowledge in ecology does not as yet give a complete explanation of water ecosystems behavior. The primary purpose of this report is to present mathematical models for the description of biogeochemical nitrogen transformations in aerobic conditions. Understanding these transformations includes examination of the basic processes as they occur simultaneously. This study also includes an examination of relationships and interactions between the main nitrogen components, improvement of the expressions for description of nitrogen transformations and finally the study of possible model applications for analyzing ecological processes in systems under controlled laboratory conditions, such as chemostat or batch systems.

An examination of models is necessary for receiving the answers to many questions raised in relation to discussions concerning the advantages and disadvantages of ecological models of great complexity. These models describe the dynamics of biological populations and their interactions with environmental factors--temperature, light, nutrients, etc. Ecological models also describe the main functions of microorganisms that define the metabolism of the population and their effects on the water environment. Various empirical functions are used for modeling microorganism dynamics. They include a number of variables, constants and specific parameters. Therefore it is necessary to understand both what the benefits are of increasing the number of state variables, and consequently the number of model

parameters, and how a reasonable choice of model structure can be made in relation to water quality studies.

In this report, the basic principles of biogeocoenosis simulation are used for describing the dynamics of biological populations. Among the functions of the microorganisms substrate uptake, metabolic excretion, and mortality are considered of major importance and especially so from the ecological point of view. This is because these functions reflect interactions between the populations and the water environment and define the biogeochemical cycling of chemical elements in the water. It is assumed that specific uptake rates of nutrients by microorganisms regulate the rates of their metabolic excretion and mortality.

The models have been constructed on the basis of conservation mass law. This means that there is a strict balance between the values of microorganism biomass and nutrient concentrations in the water environment. Reaction kinetic expressions reflect the relevant interactions between the chemical and biological components, i.e. they relate rates of microorganism substrate uptake, metabolic excretion and mortality to the nutrient content in the water.

The rates of ecological processes are defined by numerous factors that operate simultaneously. In constructing mathematical models for microorganism dynamics the maximum growth rate of the microorganisms or the maximum uptake rate of nutrients by microorganisms are usually considered as a function of temperature. The effects of other factors that reduce the maximum rates mentioned above are taken into account as a dimensionless fraction varying between 0 and 1. The influences of environmental factors are derived independently of each other. It has been assumed that plankton growth is limited by temperature, light and nutrients, while bacterial growth is determined by temperature and nutrient content.

Two mathematical models of nitrogen transformation are presented in this report. They are formulated as coupled, ordinary differential equations representing most of the nitrogen

compounds of interest in water quality studies. Oxygen was also taken into account in the models as one of the important integral characteristics of water quality. A description of all the kinetic equations for the two models considered is presented below.

3. DESCRIPTION OF MODEL NO. 1

One of the important purposes of modeling nitrogen transformation is to understand the role of plankton organisms, that is phytoplankton and zooplankton in particular, in changes of concentration in both organic and mineral nitrogen compounds. Still, it is difficult to characterize quantitatively the limiting influence of biogenic elements on plankton organisms in field conditions. Therefore, when considering nitrogen transformation in water special attention has been given to modeling the interaction between plankton organisms and the complex system of food sources. This problem is often studied in modeling eutrophication.

The state variables chosen for this model are two populations of plankton organisms; mineral forms of nitrogen--ammonium, nitrite and nitrate; dissolved organic nitrogen; nitrogenous detritus, and oxygen. Figure 1 includes these state variables and arrows connecting these variables show the relationships which are modeled.

This model differs from the model constructed by Najarian and Harleman (1975). * Firstly, the model considered here takes into account a larger number of nitrogen food sources for plankton organisms. Secondly, the metabolisms of the plankton were described by different expressions. Thirdly, oxygen was introduced into the model in order to study the nitrogen transformation effects on the oxygen regime.

The model considered studies the nitrogen transformation in batch or chemostat systems. The water volume in the

* Scheme 7 in Table 1.

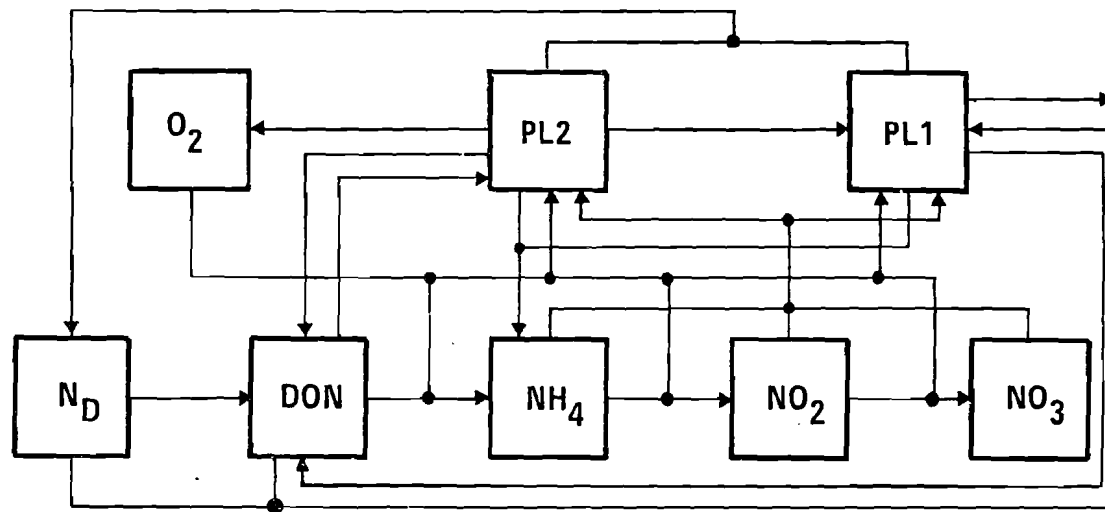


Figure 1. The block-scheme of the compound associations for Model 1.
 PL1, PL2 – the biomass of the first and second plankton groups
 DON – dissolved organic nitrogen
 NH₄, NO₂, NO₃ – the mineral nitrogen compounds:
 ammonium, nitrite and nitrate
 N_D – nitrogenous detritus
 O₂ – dissolved oxygen

experimental system is set by the parameter V. The input rate of compounds for the chemostat system is set by parameter Q (for a batch system Q = 0).

3.1 Plankton Community

It is considered that the plankton community is divided into two groups. Identification of organisms from the first plankton group (PL1) has not been made here. Any plankton organisms, such as zooplankton, protozoa and certain species of phytoplankton can be considered in this group. Therefore all nitrogen compounds may be considered as potential food sources for this population. Corrections in the scheme of feeding this plankton group may be made later when it is clear which population is identified.

The second group of plankton organisms considered (PL2) are phytoplankton. Growth of plankton organisms from both groups is controlled by the instantaneous rates of food uptake, metabolic excretion, mortality and grazing. These plankton organisms have been modeled separately because their functions differ greatly. The basic equations for the growth of plankton organisms from the two groups are:

$$\frac{dPL1}{dt} = (UP_1 - L_1 - S_1) \cdot PL1 - K_4 \cdot PL1 - (Q/V) \cdot (PL1 - PL1^0) \quad (1)$$

$$\frac{dPL2}{dt} = (UP_2 - L_2 - S_2) \cdot PL2 - P_{1PL2} \cdot PL1 - (Q/V) \cdot (PL2 - PL2^0) \quad (2)$$

where

PL1 and PL2 are biomasses in mgN/l of the first and second plankton group;

UP₁ and UP₂ are total specific uptake rates of nitrogen compounds by the same organisms (day⁻¹);

L₁ and L₂ are specific rates of metabolic excretion by the same populations (day⁻¹);

S₁ and S₂ are specific non-predation mortality rates of the same populations (day⁻¹);

K_4 is rate constant for grazing of the first plankton group by higher trophic organisms (day^{-1});

P_{1PL2} is the specific rate for grazing of the second plankton group by the first (day^{-1});

$PL1^0$ and $PL2^0$ are concentrations of plankton organisms in the inflow water for a chemostat system (mgN/ℓ).

3.1.1 Uptake of Nutrients by Plankton Organisms

Uptake of nutrients is an important factor for plankton growth; it is a very complex process. At present, expressions for uptake are not as well developed as they should be for understanding this extremely important linkage in ecosystems behavior.

The equation of Monod (Vinogradov, 1977) or the Longmuir-Hinshelwood modification of Monod's equations (Ajzatullin, 1974) are usually used for modeling nutrient uptake by various microorganisms, including plankton. In the current literature, there are many comments concerning the application of these equations to plankton growth. Some of them have been discussed by Loogman et al (1978). They noted that Monod's equation cannot describe plankton growth under transient conditions when nutrient concentration is rapidly changing. They also assumed, and presented supporting experimental evidence, that the growth of plankton depends on intracellular nutrient content.

In order to find the limiting influence of biogenic elements, on plankton growth and nitrogen in particular, it is necessary to describe the uptake rate of nutrients as a function of the nutrient content both in the water environment and in the cells. As a working hypothesis it is assumed here that:

1. nitrogen compounds taken up by plankton organisms are considered as an interchangeable food sources;
2. there is preference by plankton organisms in taking up the various nitrogen compounds;
3. the uptake rates of nitrogen compounds are dependent on a complex relationship of plankton biomass and total nitrogen content in the water environment;
4. uptake of each nitrogen source occurs simultaneously and is interdependent.

Let us consider some information concerning the uptake of nutrients by plankton organisms, namely by zooplankton and phytoplankton. The theoretical aspects of zooplankton feeding have been extensively reviewed (Saunders, 1969). In order to simulate the dynamics of zooplankton, we must determine what food sources may be utilized by zooplankton. It is generally known that phytoplankton are a primary food source for zooplankton. The majority of mathematical models take into account that phytoplankton alone are the food source for zooplankton. The information accumulated in the literature shows that simple food webs for zooplankton do not exist and not only phytoplankton, but other sources of food can be utilized by zooplankton. It was established that supplementary sources of zooplankton food may be detritus, bacteria, dissolved organic matter or any combination of these (Saunders, 1969). It is also known that very small zooplankton such as protozoa, can utilize mineral dissolved compounds (Adams, Steele, 1966; Rigler, 1969; Vinogradov, 1977).

Phytoplankton can take up organic nitrogenous compounds, such as amino-acids, urea, uric acid, etc. (Provasoli, 1963; Khailov, 1971). However, mineral nitrogen compounds are best taken up by phytoplankton. Ammonium and nitrate are taken up by phytoplankton under both dark and light conditions; however, their uptake in light is greater (Vinogradov, 1977). Assimilation of nitrite by phytoplankton is not so widely studied in comparison to ammonium and nitrate. But it is known that some of the phytoplankton species can utilize nitrite even in darkness (Grant, 1967). The mechanism of selection in taking up food sources is important not only for zooplankton but also for phytoplankton. Among mineral nitrogen compounds ammonium is considered as the best preferable food source for phytoplankton. If just the nitrite and nitrate are present in the water, then both are simultaneously assimilated by phytoplankton (Vinogradov, 1977).

A quantitative approach to the study of plankton feeding is a difficult problem. It is defined by difficulties in measuring growth and the uptake of food sources. Mathematical models may make possible the measurement and understanding of the efficiency for transformation of nutrients as food sources

for plankton organisms. An extension of the existing models which describe plankton dynamics should contribute to a scientific understanding of the mechanisms of nutrient transformation in aquatic ecosystems.

In this model, the food system for plankton organisms has been considered as highly buffered. It means that any sharp change in one food source must be compensated by others. Mineral compounds were considered as potential food sources for the first plankton group. This is due to the fact that plankton organisms of the first group are not identified and they can include organisms which have the ability to take up mineral compounds.

It is obvious that selection or preference of plankton organisms for food sources must determine the peculiarity of dynamics of both plankton organisms and its food sources (Raymont, 1963; Wilson, 1973; McNaught, et al, 1975).

Thus in the given model the total nitrogen pool for the first plankton group ($PoolN_1$) is written in the following form:

$$\begin{aligned} PoolN_1 = & d_1 \cdot PL2 + d_2 \cdot NH_4 + d_3 \cdot NO_2 + d_4 \cdot NO_3 + d_5 \cdot N_D \\ & + d_6 \cdot DON \end{aligned} \quad (3)$$

where d_{1-6} are preference coefficients. Equation (3) shows that plankton organisms from the first group can potentially utilize living matter, i.e. phytoplankton, and also the nitrogenous detritus, mineral nitrogen compounds (ammonium, nitrite and nitrate), and dissolved organic nitrogen.

The total nitrogen pool for phytoplankton ($PoolN_2$) includes mineral and organic nitrogen compounds and it can be presented by

$$PoolN_2 = d_7 \cdot NH_4 + d_8 \cdot NO_2 + d_9 \cdot NO_3 + d_{10} \cdot DON \quad (4)$$

where d_{7-10} are also preference coefficients for uptake of corresponding nutrients by phytoplankton.

It was assumed that the relation between the total nitrogen pool for growth of plankton organisms and the specific uptake rates of nitrogen compounds can be described by a modified Hinshelwood-Longmuir equation (Ajzatullin, 1974):

$$\text{for the first plankton group} \quad UP_1 = \frac{K_Z}{1 + \frac{PL_1}{POOLN_1}} \quad (5)$$

$$\text{for the second plankton group} \quad UP_2 = \frac{K_F}{1 + \frac{PL_2}{POOLN_2}} \quad (6)$$

where K_Z and K_F are actual uptake rates of nutrients by first and second plankton groups respectively. Their dimensions are day^{-1} .

Equations (5) and (6) were derived on the basis that feeding of plankton organisms depends first of all upon the concentration of available food sources and the biomass of organisms (Sushchenya, 1974), and that actually it is regulated by the ratio of the biomass concentration to food content in the water. This structure of the equation reflects the conclusion of Petipa et al (1971) that the uptake activity of plankton organisms is high at a low level of biomass. It is important that the structure of equations (5) and (6) have in any sense a comparatively low level of nutrients, while at the high nutrient level, it practically coincides with the classical Michaelis-Menten equation. In this version, all possible food sources are not subdivided into chemical and biological, and mechanisms of grazing of one biological population by the other is ignored. Also, these equations take into account all the working hypothesis mentioned above that are important for modeling plankton growth.

Using equations (5) and (6) it is possible to derive expressions for specific rates of uptake for individual compounds

by plankton organisms. The following equations characterize specific uptake rates of compounds by the first plankton (group) and phytoplankton, and are written as:

for the first plankton group

$$\text{grazing PL}_2 \quad P_{1\text{PL}_2} = \frac{K_Z \cdot d_1 \cdot \text{PL}_2}{\text{PoolN}_1 + \text{PL}_1} \quad (7)$$

$$\text{uptaking NH}_4 \quad P_{1\text{NH}_4} = \frac{K_Z \cdot d_2 \cdot \text{NH}_4}{\text{PoolN}_1 + \text{PL}_1} \quad (8)$$

$$\text{uptaking NO}_2 \quad P_{1\text{NO}_2} = \frac{K_Z \cdot d_3 \cdot \text{NO}_2}{\text{PoolN}_1 + \text{PL}_1} \quad (9)$$

$$\text{uptaking NO}_3 \quad P_{1\text{NO}_3} = \frac{K_Z \cdot d_4 \cdot \text{NO}_3}{\text{PoolN}_1 + \text{PL}_1} \quad (10)$$

$$\text{uptaking N}_D \quad P_{1\text{N}_D} = \frac{K_Z \cdot d_5 \cdot \text{N}_D}{\text{PoolN}_1 + \text{PL}_1} \quad (11)$$

$$\text{uptaking DON} \quad P_{1\text{DON}} = \frac{K_Z \cdot d_6 \cdot \text{DON}}{\text{PoolN}_1 + \text{PL}_1} \quad (12)$$

for the second plankton group

$$\text{uptaking NH}_4 \quad P_{2\text{NH}_4} = \frac{K_F \cdot d_7 \cdot \text{NH}_4}{\text{PoolN}_2 + \text{PL}_2} \quad (13)$$

$$\text{uptaking NO}_2 \quad P_{2\text{NO}_2} = \frac{K_F \cdot d_8 \cdot \text{NO}_2}{\text{PoolN}_2 + \text{PL}_2} \quad (14)$$

$$\text{uptaking NO}_3 \quad P_{2\text{NO}_3} = \frac{K_F \cdot d_9 \cdot \text{NO}_3}{\text{PoolN}_2 + \text{PL}_2} \quad (15)$$

$$\text{uptaking DON} \quad P_{2\text{DON}} = \frac{K_F \cdot d_{10} \cdot \text{DON}}{\text{PoolN}_2 + \text{PL}_2} \quad (16)$$

Thus the total specific uptake rates of nitrogen compounds by the first plankton group (UP_1) and phytoplankton (UP_2) are equal to the sum of specific uptake rates of each component:

$$UP_1 = P_{1PL2} + P_{1NH_4} + P_{1NO_2} + P_{1NO_3} + P_{1N_D} + P_{1DON} \quad (17)$$

$$UP_2 = P_{2NH_4} + P_{2NO_2} + P_{2NO_3} + P_{2DON} \quad (18)$$

At each moment of time an uptake rate for individual compounds is determined by the general nitrogen pool, the concentration of each component, and the preference coefficients. A minimum nutrient level at which uptake commences depends on the biomass of plankton organisms and nutrient content.

Such a scheme makes the model flexible and allows its use in describing the kinetics of plankton growth in a different water media and under various environmental conditions. Also, the model can be modified very easily to exclude the uptake of certain nitrogen compounds by plankton organisms for cases where consumption of some compounds is not valid. In order to do this, the respective preference coefficient must be taken equal to zero. If one introduces preference coefficients that are dependent on environmental factors the model is able to present biomass oscillations which are characteristic for successions of several species. Such oscillations are often noted during long observations of population growth under field conditions.

The actual rates of uptake of nitrogen compounds by the first plankton group (K_Z) and by phytoplankton (K_F) depends on environmental factors, mainly temperature and the intensity of light. Therefore K_Z and K_F values are modified by reduction coefficients and are written in the following form:

$$K_Z = K_1 \cdot R_{TZ} \cdot R_{IZ} \quad (19)$$

$$K_F = K_2 \cdot R_{TF} \cdot R_{IF} \quad (20)$$

where K_1 and K_2 are maximum rates of nitrogen compound uptake by the first plankton group and phytoplankton, respectively (day^{-1}); R_{TZ} and R_{TF} are reduction coefficients describing

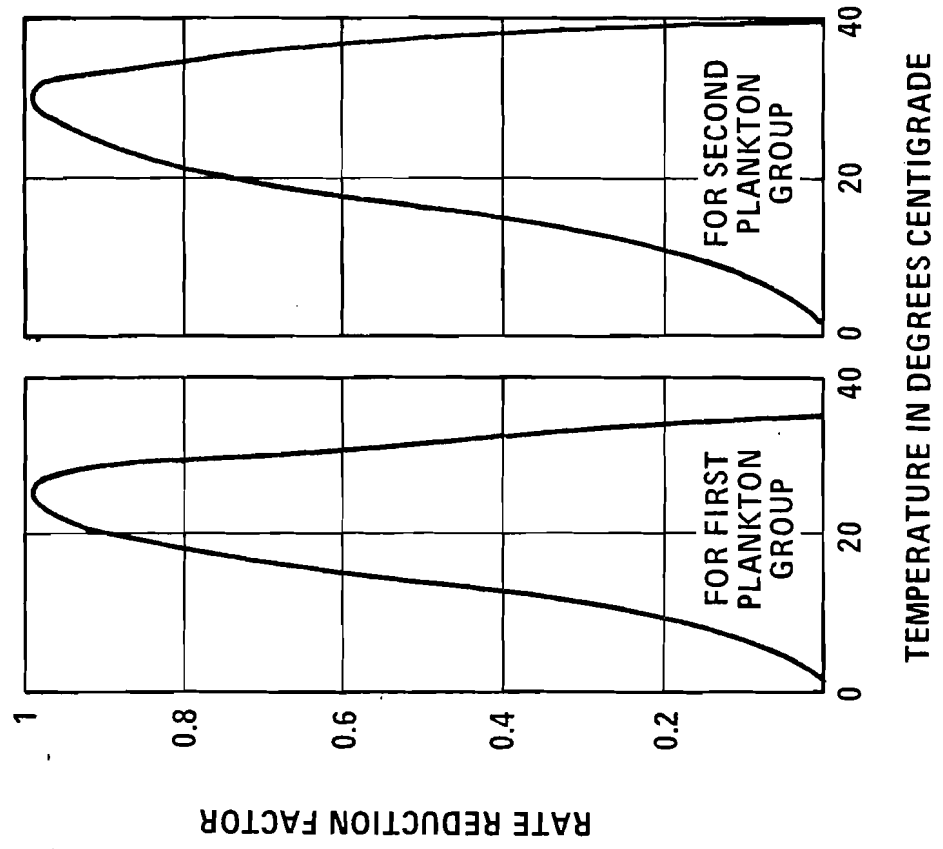


Figure 2. Uptake rate reduction with temperature for plankton organisms.

temperature dependence for the first plankton group and phytoplankton; R_{IZ} and R_{IF} are reduction coefficients describing light dependence for the first plankton group and phytoplankton. Values of reduction coefficients may vary in the range between 0 to 1.

Each type of plankton organism itself has a temperature and light dependency. Therefore this must be taken into account during modeling. Some methods of estimation for these coefficients in ecological models were recently reviewed by Fedra (1979). The simplest assumptions were applied here for description of these reduction coefficients.

It is known that generally maximum activity of zooplankton and phytoplankton takes place at 25°C and 30°C respectively. Temperature values exceeding 25°C inhibit zooplankton growth while for phytoplankton growth the temperature should not exceed 30°C (Najarian, Harleman, 1975). These temperature values were used in the model considered here for description of temperature reduction coefficients for plankton organisms. Figure 2 shows R_{TZ} and R_{TF} values as a function of temperature, if we assume that the first plankton group is comprised of zooplankton. The curves shown in Figure 2 may be represented by equations (21) and (22) as functions of temperature:

$$R_{TZ} = \frac{0.012(e^{0.317T} - 1)}{1 + 0.012 e^{0.317T}} - \frac{1.78 \cdot 10^{-7}(e^{0.484T} - 1)}{1 + 1.78 \cdot 10^{-7} e^{0.484T}} ; \quad (21)$$

$$R_{TF} = \frac{0.009(e^{0.288T} - 1)}{1 + 0.009 e^{0.288T}} - \frac{7.94 \cdot 10^{-11}(e^{0.626T} - 1)}{1 + 7.94 \cdot 10^{-11} e^{0.626T}} , \quad (22)$$

where T is water temperature in °C.

If there is additional information about the influence of temperature on the plankton organisms considered, it can be taken into account and equations (21) and (22) must be modified.

Light reduction coefficients, R_{IZ} and R_{IF} , are included in equation (19) and (20) to show how light restricts the ability of plankton organisms to achieve the maximum temperature-dependent rates of uptake of nutrients.

For simplification, it is assumed that light intensity is not of a higher optimum level for plankton development. Therefore light is described here in dimensionless units. The day is subdivided into two periods: daylight (0 - 0.5 of daytime hours) and dark (0.5 - 1 of daytime hours). Light is 0 at dark hours and 1 at noon.

It is supposed that: (1) phytoplankton takes up nutrients more actively during daylight; (2) during dark hours phytoplankton uptake of nutrients is decreased to 10%; and (3) the photosynthetic productivity of phytoplankton is absent at dark. Terms which describe R_{IF} changes during the day are shown in Table 2.

For the first plankton group it is possible to use one of three patterns in describing light reduction coefficient, R_{IZ} :

- (1) there is an influence of light on the activity of the population and it is similar to the one considered above;

Table 2. Terms describing diurnal alterations of R_{IF} .

Period of day	R_{IF} for photosynthesis	R_{IF} for uptake of nutrients
for light time (0 - 0.5)	$\sin (2 \pi t)$	$\sin (2 \pi t)$
for dark (0.5 - 1)	0	0.1

where t is the time given (for the period of a day)

- (2) there is an influence of light but it is the reverse of that considered above;
- (3) there is no influence of light on the activity of organisms of the first plankton group.

Terms for description of these patterns are presented in Table 3.

Changes of light reduction coefficients during the day, according to assumptions used in model, are given in Figure 3. The influence of light on fresh-water zooplankton is often not taken into account during modeling. In this case if plankton from the first group is considered as zooplankton, then R_{IZ} may be taken to be 1 (Pattern 3, Table 3). The second pattern may be used to explain an assumption that zooplankton which migrate into the euphotic zone at night feed only during the hours of local darkness. This type of light influence on zooplankton activity was used by Najarian and Harleman (1975). The first pattern may be used if the first plankton group is considered as phytoplankton.

Table 3. Terms describing diurnal alterations of R_{IZ} .

Period of day	First pattern R_{IZ}	Second pattern R_{IZ}	Third pattern R_{IZ}
for light time (0 - 0.5)	$\sin (2 \pi t)$	0.1	1
for dark (0.5 - 1)	0.1	$0.1 + 0.9 \sin (\pi + 2\pi t)$	1

here t is the time given (for the period of a day).

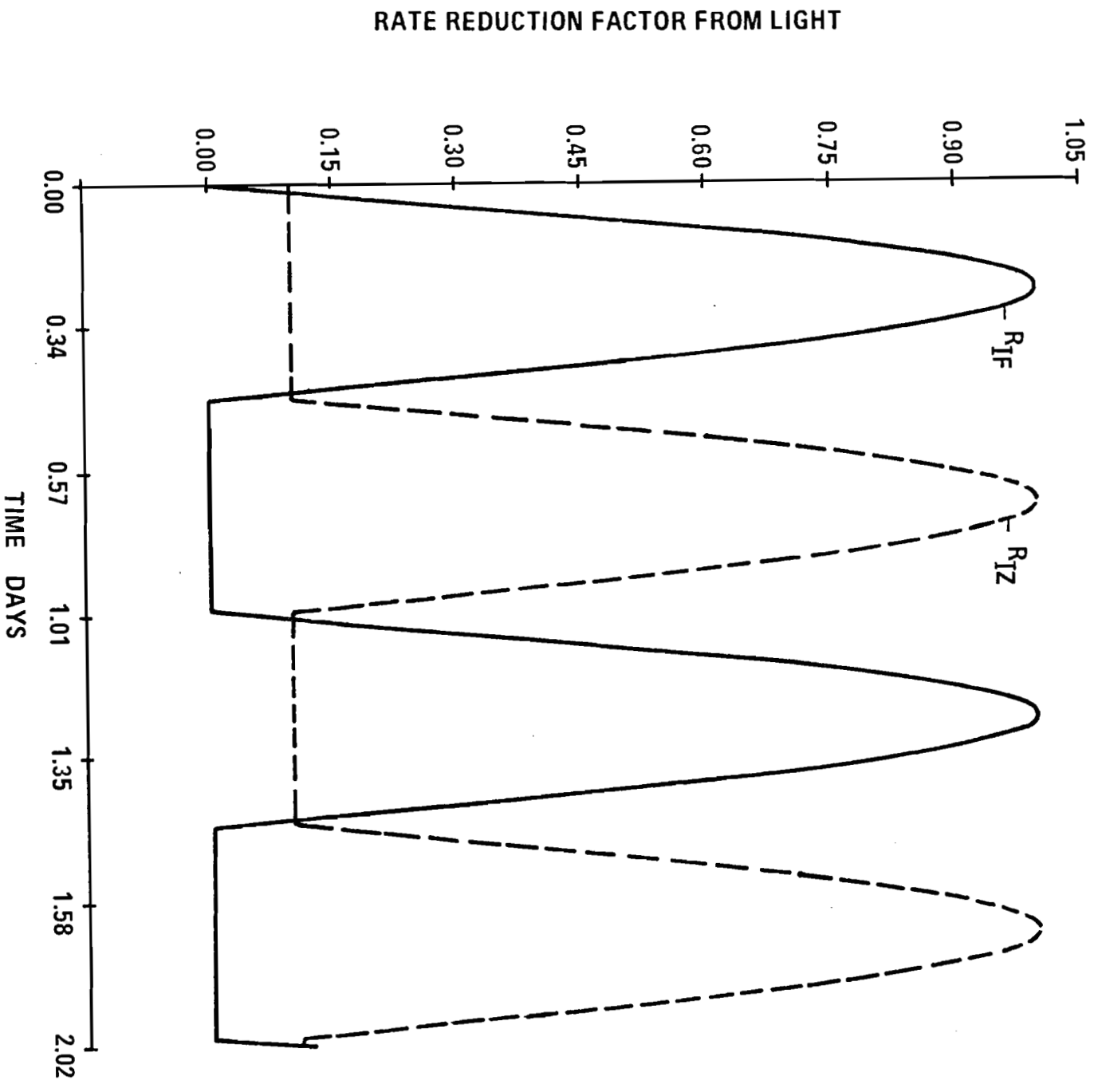


Figure 3. Diurnal fluctuation of uptake rate reduction factors from light for first plankton group (R_{IF}), second pattern, Table 3) and for second plankton group (R_{IZ}).

3.1.2 Plankton Excretions

The initial hypothesis is that excretion of plankton organisms would directly reflect changes in feeding conditions. The specific rates of metabolic excretion by plankton organisms (L_1 and L_2) are considered to be a fraction of uptake rates and are given by:

$$L_1 = r_1 \cdot UP_1 \quad (23)$$

$$L_2 = r_2 \cdot UP_2 \quad (24)$$

where r_1 and r_2 are coefficients of excretion activity for the first plankton group and for phytoplankton, respectively. They are specific for each type of organism. Sometimes a fraction of the metabolic product excretion for plankton organisms is considered as a constant value (Bloomfield et al, 1973). Obviously during plankton growth this fraction is altered (LaRow et al, 1975; Jawed, 1973; Saunders, 1969) because the food concentration is changing. It is possible to assume that it depends simultaneously on the quality and quantity of food, and on the total specific uptake rate. This is confirmed by experimental observations on plankton organisms (Gaevskaya, 1958; Petipa, et al, 1974).

Extensive literature on biological data concerning micro-organism metabolism shows that each population increases its level of excreted metabolic products when the content of nutrients in the water environment is limited. When feeding conditions become favorable, then this fraction begins to increase (Petipa, et al, 1974). Therefore a convenient structure of the equation for description of this pattern of microorganism behavior is

$$r_i = \frac{\frac{a_j}{a_{j+1}} \cdot UP_i}{\frac{1}{a_{j+1}} + UP_i} + \left(1 - \frac{a_j}{a_{j+1}}\right) \quad (25)$$

or

$$r_i = \frac{\omega \cdot UP_i}{P' + UP_i} + (1 - \omega) \quad (25a)$$

where UP_i is the specific uptake rate, ω is the ratio of coefficients a_j/a_{j+1} , P' is $1/a_{j+1}$. The term $(1-\omega)$ in the equation (25a) indicates the minimal level of excreted metabolic products when nutrients are limited. In other words this minimal level is sufficient for maintenance of the microorganisms' activity in unfavorable feeding conditions. The maximum possible level of excretion is 1 when the uptake rate reaches a given high value. Equation (25a) demonstrates that minimal level of excretion, $(1-\omega)$, is increased by $\omega/2$ when the uptake rate equals P' .

Therefore r_1 and r_2 values for equations (23) and (24) respectively have been formulated in this model as

$$r_1 = \frac{a_1 \cdot UP_Z}{1 + a_2 \cdot UP_Z} + (1 - \frac{a_1}{a_2}) \quad (26)$$

$$r_2 = \frac{a_3 \cdot UP_F}{1 + a_4 \cdot UP_F} + (1 - \frac{a_3}{a_4}) \quad (26a)$$

where coefficients a_j have the dimensions (day). Absolute values of the coefficients a_j regulate the time at which the microorganism biomass peak occurs while the ability of the microorganism to excrete metabolic products during growth depends on ratio a_j/a_{j+1} .

Equations (25-26a) are a modified form of Ivlev's expression which is widely used for the description of plankton metabolism (Sushchenya, 1971). Previously, a similar equation was applied

for simulation of the excretion activity of bacteria (Ajzatullin, Leonov, 1975b; Leonov, Ajzatullin, 1975b) and protozoa (Leonov, Ajzatullin, 1978).

3.1.3 Plankton Mortality

Mortality of plankton organisms considered in this model includes their non-grazing elimination and grazing by organisms of the next trophic level. The following equations were used for description of specific non-predation mortality rates for plankton groups:

$$S_1 = g_1 + g_2 \cdot r_1 \quad (27)$$

$$S_2 = g_3 + g_4 \cdot r_2 \quad (28)$$

where g_i are constants that have dimensions day^{-1} .

These equations show that specific mortality rates depend on plankton activities and thus are conditioned by nutrition. In other words there are certain constant rates for plankton elimination (g_1 for the first plankton group and g_3 for phytoplankton) when the concentration of nutrients is limited. When nutrient concentration increases the organism activity also intensifies and specific rates of mortality of plankton become higher. This type of organism response depends on the values of the g_2 and g_4 coefficients for the first plankton group and for phytoplankton respectively.

3.2 Detritus

It is assumed that nitrogenous detritus is formed from dead plankton organisms. The quantity of detritus formed is proportional to the biomass of the plankton organisms. Detritus decomposition to dissolved organic nitrogen is taken into consideration in the model. This process is described by the first-order kinetics. Uptake of detritus by a mixed plankton community is included in the general scheme of nitrogen transformations.

Thus the dynamics of nitrogenous detritus is described by:

$$\frac{dN_D}{dt} = g_6 \cdot S_2 \cdot PL2 + g_7 \cdot S_1 \cdot PL1 - K_5 \cdot N_D - P_{1N_D} \cdot PL1 - (Q/V) \cdot (N_D - N_D^O) \quad (29)$$

where g_6 and g_7 are coefficients; K_5 is the first order rate constant of detritus decomposition to dissolved organic nitrogen; N_D^O is the detritus content in the inflow water for a chemostat system; P_{1N_D} is defined above.

3.3 Nitrogen compounds

Dissolved organic nitrogen (DON), ammonium (NH_3), nitrite (NO_2) and nitrate (NO_3) are the major components of the nitrogen system and are included in the given model. Stepwise transformation of these compounds, DON to NH_3 , NH_3 to NO_2 , NO_2 to NO_3 , in natural waters depends on bacterial activity. For simplification in this model the kinetics of these transformations are assumed to be first-order reactions as in scheme 1 (Ajzatullin, 1967; Mijake, Wada, 1968) and 8 (Najarian, Harleman, 1975) shown in Table 1.

According to assumptions used in model construction, dissolved organic nitrogen and mineral nitrogen forms are taken up by plankton organisms. The concentration of DON in the water is compensated by the decomposition of the detritus and by photosynthetic production of phytoplankton. The excretion products of plankton organisms included in the equations are the dissolved organic nitrogen and ammonium. Fractions of these products excreted by plankton during metabolism may be changed according to information for plankton organisms accounted for during the simulation.

The equations describing the dynamics of chemical nitrogen compounds have the following forms:

$$\begin{aligned} \frac{dDON}{dt} = & K_5 \cdot N_D - K_3 \cdot DON + g_5 \cdot L_F \cdot PL2 + (1 - g_{22}) \cdot L_2 \cdot PL2 \\ & + (1 - g_{23}) \cdot L_1 \cdot PL1 - P_{1DON} \cdot PL1 - P_{2DON} \cdot PL2 \\ & - (Q/V) \cdot (DON - DON^O) \end{aligned} \quad (30)$$

$$\begin{aligned} \frac{dNH_4}{dt} = & K_3 \cdot DON - K_6 \cdot NH_4 - P_{1NH_4} \cdot PL1 - P_{2NH_4} \cdot PL2 \\ & + g_{22} \cdot L_2 \cdot PL2 + g_{23} \cdot L_1 \cdot PL1 - (Q/V) \cdot (NH_4 - NH_4^O) \end{aligned} \quad (31)$$

$$\begin{aligned} \frac{dNO_2}{dt} = & K_6 \cdot NH_4 - K_7 \cdot NO_2 - P_{1NO_2} \cdot PL1 - P_{2NO_2} \cdot PL2 - \\ & - (Q/V) \cdot (NO_2 - NO_2^O) \end{aligned} \quad (32)$$

$$\frac{dNO_3}{dt} = K_7 \cdot NO_2 - P_{1NO_3} \cdot PL1 - P_{2NO_3} \cdot PL2 - (Q/V) \cdot (NO_3 - NO_3^O) \quad (33)$$

where

- K_3 is first-order rate constant for decomposition of DON to NH_4 (day^{-1});
- K_6 is first-order rate constant for oxidation of NH_4 to NO_2 (day^{-1});
- K_7 is first-order rate constant for oxidation of NO_2 to NO_3 (day^{-1});
- L_F is the specific rate of photosynthetic production of organic nitrogen by phytoplankton (day^{-1});
- g_{22} and g_{23} are coefficients for the fractions of ammonium excretion by phytoplankton and the first plankton group (dimensionless);
- g_5 is the DON fraction released by phytoplankton during photosynthesis (dimensionless);
- DON^O , NH_4^O , NO_2^O and NO_3^O are concentrations of nitrogen compounds in the inflow water for a chemostat system (all mgN/l).

In this model first-order rate constants for stepwise nitrogen transformations ($K_3 - K_7$) are assumed to be temperature dependent. Equations for temperature correction of these constants and their values are presented in Table 4. The change of rate constant values, due to temperature variations, is shown in Figure 4.

3.4 Oxygen

The oxidation transformation of nitrogen compounds in water is accompanied by oxygen consumption. Usually an additional term is introduced into the Streeter-Phelps model for estimating oxygen expenditure for nitrogen compound oxidation (Dobbins, 1964). Models constructed from Streeter-Phelps assumptions have no detailed description of nitrogen compound transformation. This type of model only takes into account general oxygen removal for mineral compound oxidations (nitrification). However, the phytoplankton activity provides oxygen enrichment of water. In laboratory conditions, i.e. chemostat systems, the oxygen content does not limit the development of microorganisms and oxidation processes because the aerobic conditions are always maintained by artificial aeration.

By means of modeling plankton dynamics it is possible to estimate values for oxygen consumption in oxidizing individual nitrogenous compounds and plankton respiration.

The possibilities for mathematical modeling of the oxygen regime have been studied by many authors. Recently, a detailed review of these studies has been made by Ajzatullin and Lebedev (1977). However, at present there are substantial difficulties in modeling the rates of oxygen production, especially when the pollutant concentration is high (Vinberg, 1973).

Studies conducted show that rates of oxygen production in heavily polluted water are similar to the rates of atmospheric re-aeration (Nusbaum, Miller, 1952), or, during some seasons, even higher (Knopp, 1960 and 1966).

Table 4. Rate constants and equations for temperature corrections.

REACTIONS	TEMPERATURE DEPENDENCE FOR RATE CONSTANTS	AUTHORS
$\text{DON} \xrightarrow{K_3} \text{NH}_4$	$K_3 = K_3(0^\circ\text{C}) \cdot T$ $K_3(0^\circ\text{C}) = 0.007$	Najarian, Harleman, 1975
$\text{ZO} \xrightarrow{K_4} \text{grazing by higher organisms}$	$K_4 = K_4(20^\circ\text{C}) \cdot 1.05^{(T - 20)}$ $K_4(20^\circ\text{C}) = 0.1$	in given report
$\text{N}_D \xrightarrow{K_5} \text{DON}$ $\text{NH}_4 \xrightarrow{K_6} \text{NO}_2$ $\text{NO}_2 \xrightarrow{K_7} \text{NO}_3$	$K_i = K_i(20^\circ\text{C}) \cdot 1.05^{(T - 20)}$ $K_5(20^\circ\text{C}) = 0.05$ $K_6(20^\circ\text{C}) = 0.2$ $K_7(20^\circ\text{C}) = 0.35$	Najarian, Harleman, 1975

T = Temperature in degrees Centigrade.

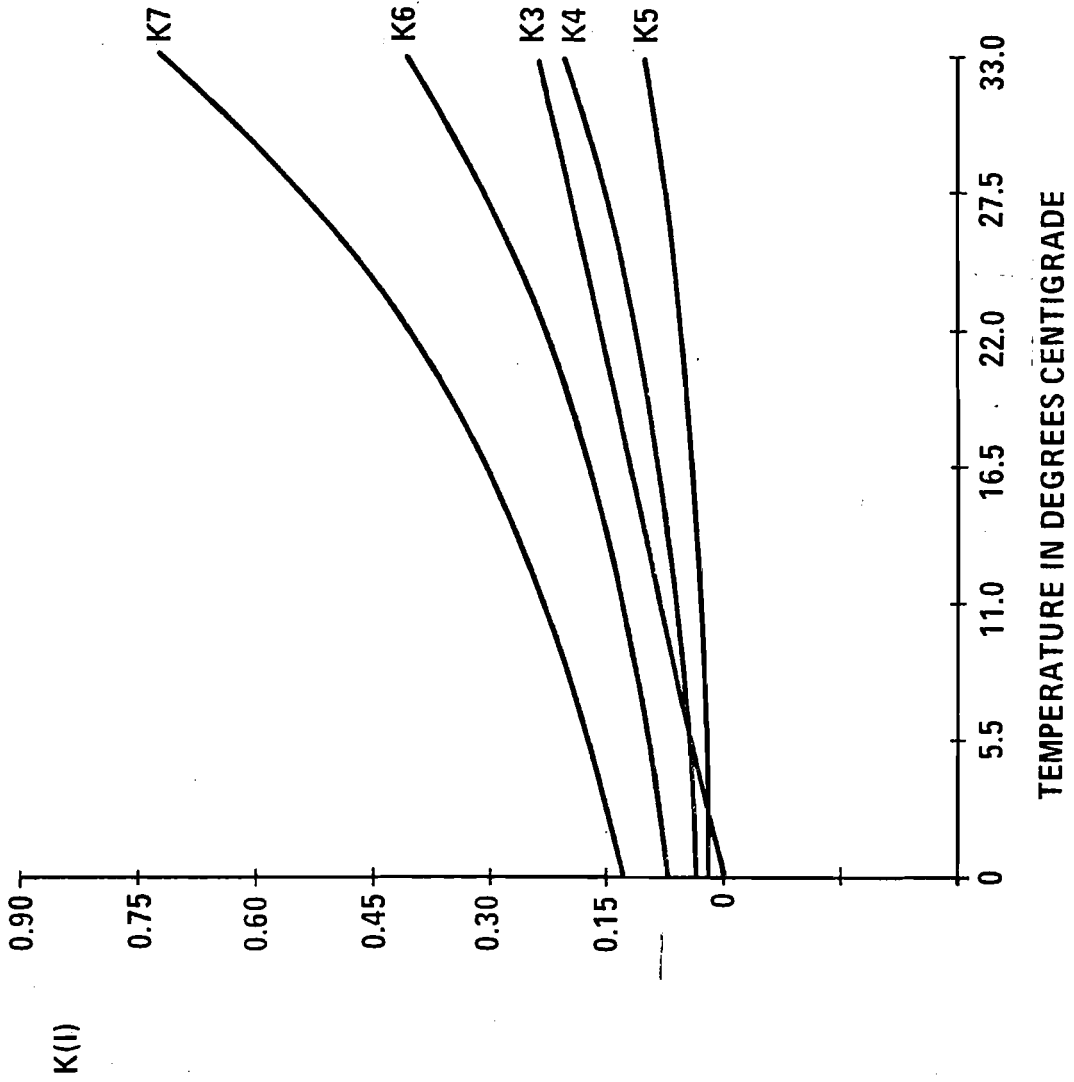


Figure 4. Temperature dependence for rate constants of Model I.

Thus, the role of photosynthetic aeration cannot be disregarded in modeling water ecological systems. Without this factor, it is impossible to: (1) receive accurate estimates for the self-purification capacity of water bodies; (2) have information on actual rates of chemical compound transformation; and (3) describe the true oxygen regime of water bodies.

In the present model the oxygen content was included together with the concentrations of the nitrogenous compounds mentioned above. The equation for oxygen dynamics can be written as follows:

$$\begin{aligned} \frac{dO_2}{dt} = & V_{O_2} \cdot PL_2 - g_8 \cdot g_9 \cdot DON - g_{10} \cdot g_{11} \cdot NH_4 - g_{12} \cdot g_{13} \cdot NO_2 \\ & - g_{14} \cdot g_{15} \cdot L_2 \cdot PL_2 - g_{16} \cdot g_{17} \cdot L_1 \cdot PL_1 \\ & - (Q/V)(O_2 - O_2^{sat}) - g_{20}(O_2 - O_2^{sat}), \end{aligned} \quad (34)$$

where

$g_8, g_{10}, g_{12}, g_{14}, g_{16}$ are optional coefficients;
 $g_9, g_{11}, g_{13}, g_{15}, g_{17}$ are stoichiometric coefficients;
 g_{20} is rate of atmospheric re-aeration (day^{-1});
 V_{O_2} is the rate of photosynthetic production of oxygen by phytoplankton ($\text{mg } O_2/\text{mg N/day}$);
 O_2^{sat} is the saturation oxygen concentration ($\text{mg } O_2/\ell$).

Thus, in the given model oxygen concentration is determined by processes of atmospheric re-aeration, biochemical oxidation of nitrogenous compounds, of plankton respiration and photosynthesis.

Detailed theoretical studies have been recently conducted for modeling processes of atmospheric re-aeration (Kondratjuk, 1977; Negulescu, Rojanski, 1969; Isaacs, Gaudy, 1968) as well as for studying experimentally the magnitude of re-aeration constants (Isaacs, Gaudy, 1968). The simplest method was used

here in describing the process of atmospheric re-aeration. It is assumed that in laboratory conditions, only temperature significantly affects re-aeration. Therefore, in describing the rate of atmospheric re-aeration, temperature dependence has been included (Isaacs, Gaudy, 1968):

$$g_{20} = g_{21} \cdot \theta^{(T - 20)} , \quad (35)$$

where θ is the temperature coefficient, g_{21} is the rate constant of re-aeration at 20°C . The coefficient values for θ and g_{21} were taken equal to 1.05 and 1.25 respectively (Sornberger, Keshavan, 1973). In modeling ecological water systems, values for g_{21} can be also correlated with environmental factors, such as flow-rate, oxygen diffusion, slope, depth of water, etc. (Kondratjuk, 1977; Negulescu, Rojanski, 1969; Isaacs, Gaudy, 1968).

Experimental methods for determining virtual re-aeration coefficients have made it possible to reduce to a minimum the influence of such important factors as BOD, photosynthesis, and respiration (Kondratjuk, 1977). Thus, the rate of atmospheric re-aeration has been established as a function of the re-aeration constant (corrected for temperature), g_{20} , and by the difference between oxygen saturation concentration (O_2^{sat}) and its actual concentration (O_2). The saturation oxygen content can be calculated to a precision of ± 0.01 mg O_2/ℓ by the polynomial function (Wang L., Wang Mu, 1976):

$$O_2^{\text{sat}} = 14.61996 - 0.4042T + 0.00842T^2 - 0.00009T^3 , \quad (36)$$

where T is the temperature in $^{\circ}\text{C}$. Temperature change during the day is described by the sinusoidal function:

$$T^{\circ}\text{C} = T_{\text{av}} + A \cdot \sin (2 \pi t) \quad (37)$$

where t is the fractional part of the day, T_{av} is daily average temperature, A is the amplitude of temperature fluctuation during the day.

There is a close correlation between photosynthesis and growth of plankton (Talling, 1955). Therefore, we can represent the photosynthetic production of oxygen by the same function that describes plankton growth. The metabolic and photosynthetic excretion of plankton are assumed to be equivalent during the daytime. The specific rates of metabolic (L_1) and photosynthetic (L_F) plankton excretion for the period 0 - 0.5 day are also the same. In the dark part of the day (the period 0.5 - 1) the specific rate of plankton metabolic liberation considerably decreases (to 10%), while the process of photosynthesis completely stops (Table 3). L_F values, indirectly connected with plankton growth, are included in the Michaelis-Menten type of equation, which is used for describing the photosynthetic production of oxygen. Thus, the specific rate of photosynthetic oxygen production is written as follows:

$$V_{O_2} = \frac{g_{18} \cdot L_F}{1 + g_{19} \cdot L_F} \quad , \quad (38)$$

where g_{18} is a coefficient with dimensions ($\text{mg O}_2/\text{mgN}$); g_{19} has the dimension (day).

The classification of all constants used in Model 1 is shown in Table 5 in accordance with the purpose of their application. Model 1 has 43 constants and requires 8 initial concentrations of compounds.

4. SIMULATION RUNS AND DISCUSSION

The purpose of the application of model 1 in this report is examination of the equations that describe the uptake of nutrients by plankton organisms. It is necessary because of a modified structure of the equations for description of feedback and interactions between the biotic components and nutrient

Table 5. Main functions of the constants in Model 1.

Parameters for description of	Preference coefficient for different nitrogenous matter	Coefficients for physiological activity of plankton	Stoichiometric constants for calculations of oxygen consumption	Optional constants
<u>Substrate Uptake</u>	For first plankton group	For first plankton group		
K ₁ - by first plankton group	d ₁ - grazing PL2	a ₁ } liberation of	g ₉ - oxidation DON	g ₆
K ₂ - by phytoplankton	d ₂ - consumption NH ₄	a ₂ } metabolic	g ₁₁ - oxidation NH ₄	g ₇
<u>Chemical Reactions</u>	d ₃ - consumption NO ₂	g ₂₃ } products	g ₁₃ - oxidation NO ₂	g ₈
K ₃ - DON → NH ₄	d ₄ - consumption NO ₃	g ₁ } mortality	g ₁₅ } plankton	g ₁₀
K ₅ - N _D → DON	d ₅ - consumption N _D	g ₂ } mortality	g ₁₇ } respiration	g ₁₂
K ₆ - NH ₄ → NO ₂	d ₆ - consumption DON	For second plankton group		g ₁₄
K ₇ - NO ₂ → NO ₃	For second plankton group	a ₃ } liberation of		g ₁₆
<u>Ecological Process</u>	d ₇ - consumption NH ₄	a ₄ } metabolic		g ₂₄
K ₄ - grazing PL1	d ₈ - consumption NO ₂	g ₂₂ } products		
<u>Physical Processes</u>	d ₉ - consumption NO ₃	g ₃ } mortality		
g ₂₀ } atmospheric	d ₁₀ - consumption DON	g ₄ } mortality		
g ₂₁ } re-aeration		g ₁₈ } photosynthetic		
		g ₁₉ } production of		
		g ₅ } oxygen and organic matter		

pools used in this model. In simulation runs model 1 is used for studying nitrogen transformations and the influence of plankton on the rates of nitrogen matter changes in a hypothetical situation.

These special cases will provide some theoretical understanding of the behavior of the nitrogen system, the elemental dynamics of which is described by the set of equations of model 1.

In simulation runs the first plankton group was assumed to be zooplankton. For all cases considered below the fixed values of the preference coefficients, d_i , are used. They are presented in Table 6.

Values of the d_i coefficients were chosen after several simulation runs. For simplification, the uptake of DON by plankton organisms is not taken into account in this set of runs and corresponding values for the preference coefficients are therefore zero (Table 6). The chosen values of the d_i coefficients show that the preference of the first plankton group for different nitrogen sources can be expressed by the following ratios*:

$$N_D : NH_4 : PL2 : NO_2 : NO_3 = 8 : 6 : 4 : 4 : 1$$

The same ratios for phytoplankton are

$$NH_4 : NO_2 : NO_3 = 5 : 1.25 : 1.$$

These ratios show that if the concentrations of all the nitrogen sources could be equal to each other, then the rates of their uptake by plankton organisms would be proportional to the d_i values.

* Uptake of mineral nitrogen compounds by the first plankton group is considered here as a hypothetical case.

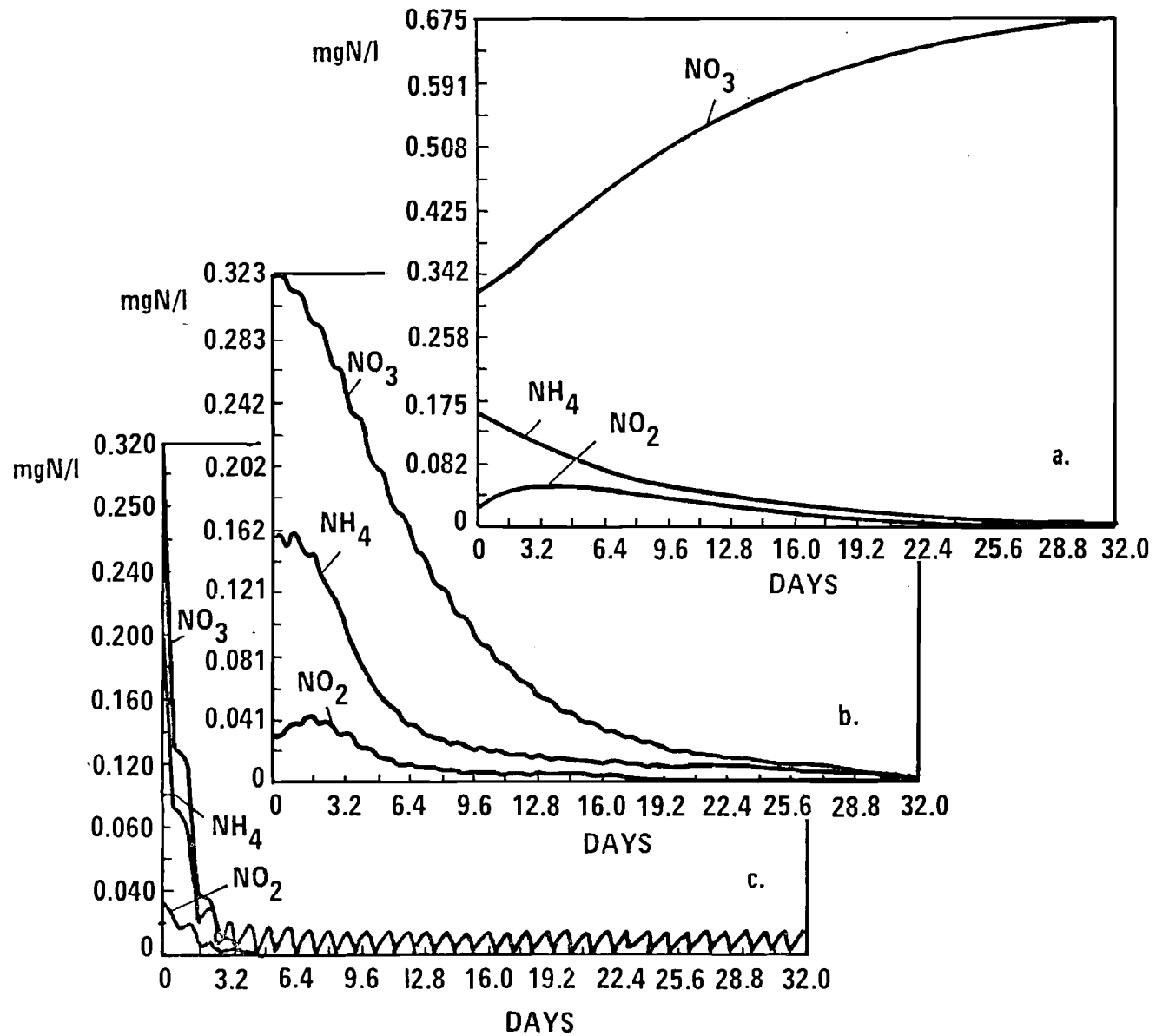


Figure 5. Modeling of the nitrogen transformations in batch systems with the help of Model 1.
 a. without plankton
 b. in presence of plankton from First group
 c. in presence of plankton from Second group

Table 6: Values of the preference coefficients used in modeling

Nitrogen compounds	For first plankton group						For phytoplankton			
	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆	d ₇	d ₈	d ₉	d ₁₀
Phytoplankton	0.1	-	-	-	-	-	-	-	-	-
Ammonium	-	0.15	-	-	-	-	0.2	-	-	-
Nitrite	-	-	0.1	-	-	-	-	0.05	-	-
Nitrate	-	-	-	0.025	-	-	-	-	0.04	-
Detritus	-	-	-	-	0.2	-	-	-	-	-
Dissolved organic nitrogen	-	-	-	-	-	0.0	-	-	-	0.0

Figure 5 shows the results of the first set of simulation runs*. Initial values of the nitrogen compound concentrations used in these runs are presented in Table 7. Initial values of the nitrogen concentrations and some values for the rate constants of chemical nitrogen transformation were taken from the report by Najarian and Harleman (1975). Values of all the constants used for these simulations are presented in Table 8.

The comparatively high values of the maximum uptake rates, K_1 and K_2 , were assumed arbitrarily for the simulation runs to examine how the modified structure of the equations for uptake are dynamic and to compare its performance with the classical Michaelis-Menten approach. In fact, values of K_1 and K_2 in equations (7) - (16) are corrected by multipliers, i.e. the preference coefficients d_i , to regulate the uptake rates of each compound.

* A constant time step of 0.1 day was used for the numerical solution of equations of model 1 by the Runge-Kutta-4 method.

Table 7: Initial values of nitrogen compounds for Model 1 in Figure 5

Nitrogen Compounds	Initial values for nitrogen compounds in mg/ℓ		
	run 22	run 23	run 24
DON	0.11	0.11	0.11
NH ₄	0.16	0.16	0.16
NO ₂	0.03	0.03	0.03
NO ₃	0.32	0.32	0.32
PL1	0.02	0	0
PL2	0	0	0.093
N _D	0.11	0.11	0.11

Parameters	Values	Parameters	Values	Parameters	Values	Parameters	Values	Parameters	Values
K ₁	30	a ₁	0.45	g ₄	0.08	g ₁₁	3.43	g ₁₈	48
K ₂	100	a ₂	0.5	g ₅	0.3	g ₁₂	1	g ₁₉	0.3
K ₃	0.007	a ₃	0.45	g ₆	1	g ₁₃	1.14	g ₂₀	0
K ₄	0.1	a ₄	0.5	g ₇	1	g ₁₄	0.1	g ₂₁	0
K ₅	0.05	g ₁	0.18	g ₈	0.4	g ₁₅	13.35	g ₂₂	0.7
K ₆	0.2	g ₂	0.12	g ₉	13.35	g ₁₆	0.1	g ₂₃	0.7
K ₇	0.35	g ₃	0.15	g ₁₀	1	g ₁₇	13.35	g ₂₄	0

Table 8. Rate constants for Model 1 in Figure 5.

The next important part of the model structure is the excretion activity of the plankton organisms. It is assumed that coefficients which describe excretion activity of the first plankton group and phytoplankton are similar, i.e. $a_1 = a_3 = 0.45$ and $a_2 = a_4 = 0.5$ (Table 8). These values show that plankton activity during nutrient limitation is determined by the ratios a_1/a_2 and a_3/a_4 (equations (26) and (26a)) and for both plankton populations this activity is 0.1. Special experiments are necessary for a precise estimation of the a_i values for each plankton group.

At each moment of time, the maximum activity of both plankton populations is determined by the combined efforts of temperature, light and nutrients. The second pattern of light influence on the first plankton group (Table 3) was used for these simulation runs.

The time period chosen for these mathematical runs was 32 days. The temperature change during each of the 32 days was assumed to be invariable and values of T_{av} and A in equation (37) were taken to be equal 20°C and 5°C respectively.

The model describes the consecutive oxidative transformation* of nitrogen compounds when plankton organisms are absent in the system. In this case, the results do not generally differ from those obtained by Harleman (1978). The analysis of the models, constructed on the basis of kinetic equations of first-order reactions, was discussed in detail by Harleman (1978) and therefore the possibilities of such models are only briefly reviewed here.

Changes of mineral nitrogen compounds in a laboratory batch system (without plankton) is shown in Figure 5a. Comparison of these results with the results obtained by Harleman (1978) for purely chemical models allows some generalizations to be made. Firstly, such models represent consecutive transformations of nitrogen compounds and accumulation of the final transformation

* Kinetics of first-order reactions

product, namely nitrate. Secondly, the concentration of nitrogen compounds always achieves a steady state when the model uses the equations of first-order reactions. Moreover, the time necessary for reaching such steady states is determined by the initial concentrations and rate constants. Taking into account the temperature fluctuation during the day, the time for reaching steady-state conditions increases. Thirdly, the results show that the concentrations of all compounds change smoothly and without sharp oscillation.

The hypothetical influence of a zooplankton population on the dynamics of mineral nitrogen compounds is shown in Figure 5b. Oscillations in the mineral nitrogen compounds are caused by daily fluctuations in the zooplankton population. In this case, no accumulation of the final product of the nitrogen transformations (nitrate) takes place, and all mineral nitrogenous compounds reach steady-state concentrations approximately after 25 days.

The presence of phytoplankton in the system considerably changes the nitrogen transformations (Figure 5c). Compound concentrations reach stationary levels on the fourth day. During the first days, the content of mineral matter quickly decreases and after the third day only small fluctuations of ammonium are observed; these fluctuations result from the diurnal activity of phytoplankton. In the system with phytoplankton, concentrations of nitrite and nitrate are one order-of-magnitude less than in the system with zooplankton.

Figure 6 shows results for the chemostat system.* The initial concentrations for each compound are presented in Table 9. The same concentrations for the nitrogen compounds were used by Najarian, Harleman (1975) in modeling nitrogen turnover in natural water. Values for rate constants were taken from Table 8. In the chemostat system the concentrations of dissolved organic nitrogen and ammonium were assumed to be comparatively high-- 2mg/l and 5 mg/l, respectively (Table 9). The temperature was considered constant (20°C) throughout the whole experiment (32 days).

* The ratio Q/V was taken to be equal 0.774 for this run.

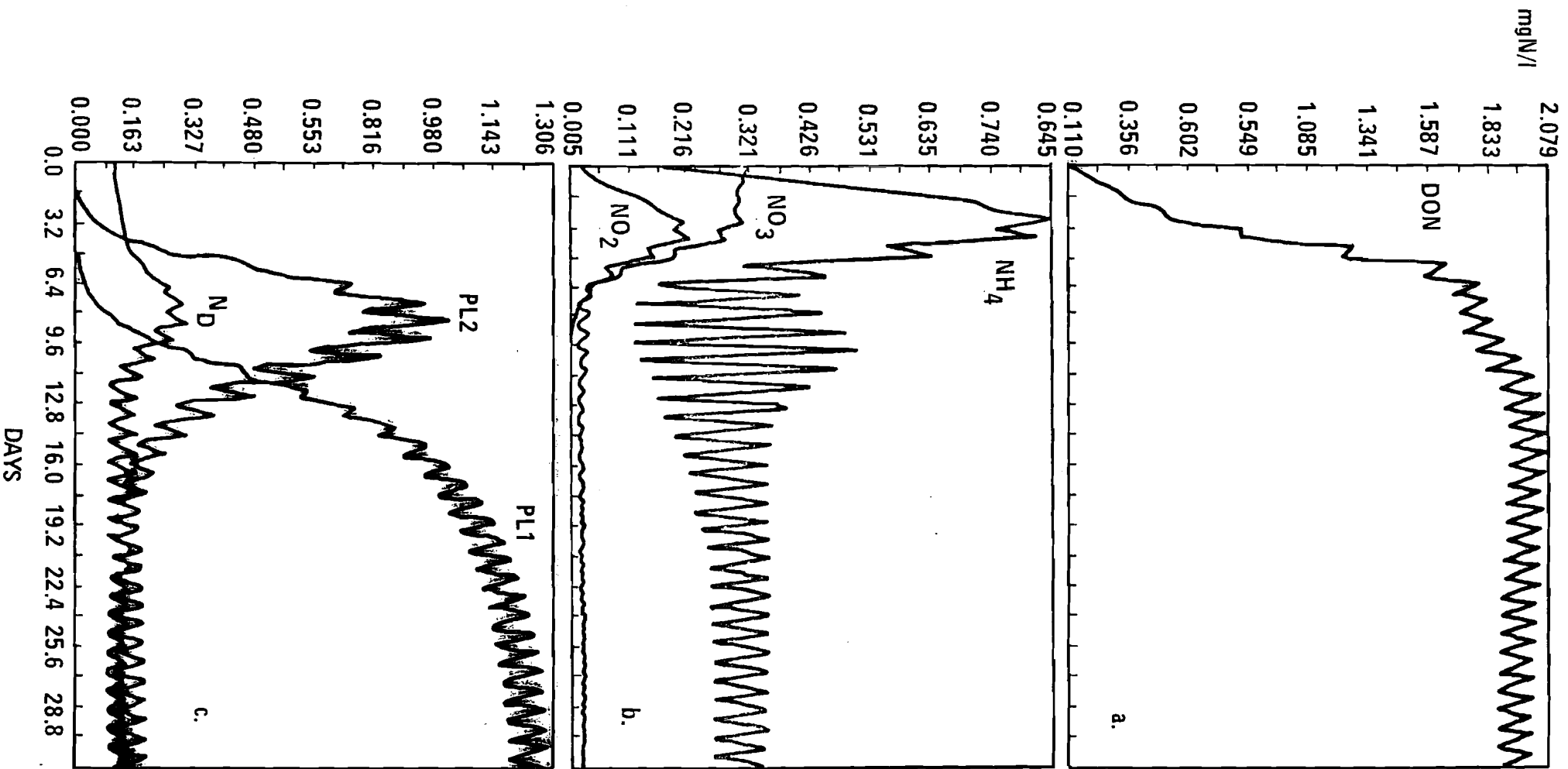


Figure 6. Modeling of the nitrogen transformations in chemostat system with the help of Model 1. Concentration changes of nitrogen compounds: a. DON, b. NH₄, NO₂, NO₃, c. N_D, PL1, PL2.

Table 9: Initial concentrations of nitrogen compounds for Model 1 in Figure 6

Initial Concentrations of Nitrogen Compounds (mg/ℓ)	Concentration of Nitrogen Compounds in Inflow Water (mg/ℓ)
DON = 0.11 NH ₄ = 0.16 NO ₂ = 0.03 NO ₃ = 0.32 PL1 = 0 PL2 = 0 N _D = 0.11	DON = 2.0 NH ₄ = 5.0 NO ₂ = 0.05 NO ₃ = 0.002 PL1 = 0.002 PL2 = 0.03 N _D = 0.2

Simulation results show that the concentration of dissolved organic nitrogen increases in the first two days and stabilizes after the 15th day (Figure 6a). Small fluctuations at the steady-state level depend on the photosynthetic activity of plankton.

The dynamic variations of the mineral nitrogen compounds are shown in Figure 6b. During the first three days the ammonium content increases and then begins to decrease. Most amplitude fluctuations in the ammonium content were observed during the period from the 6th to the 10th day, due to plankton activities, especially phytoplankton. The nitrite concentration has an intermediate maximum occurring between the 3rd and 5th days, and after that the nitrate content falls. It stabilizes by the 10th day at a comparatively low level (approximately 0.006 mg/ℓ).

During the first 3 to 4 days, the nitrate content changes slowly. Then on the 4th to 6th days, when the phytoplankton begin intensive growth, nitrate begins to decrease rapidly. After the 8th day the nitrate content stabilizes (0.08 mg/ℓ) with small oscillations.

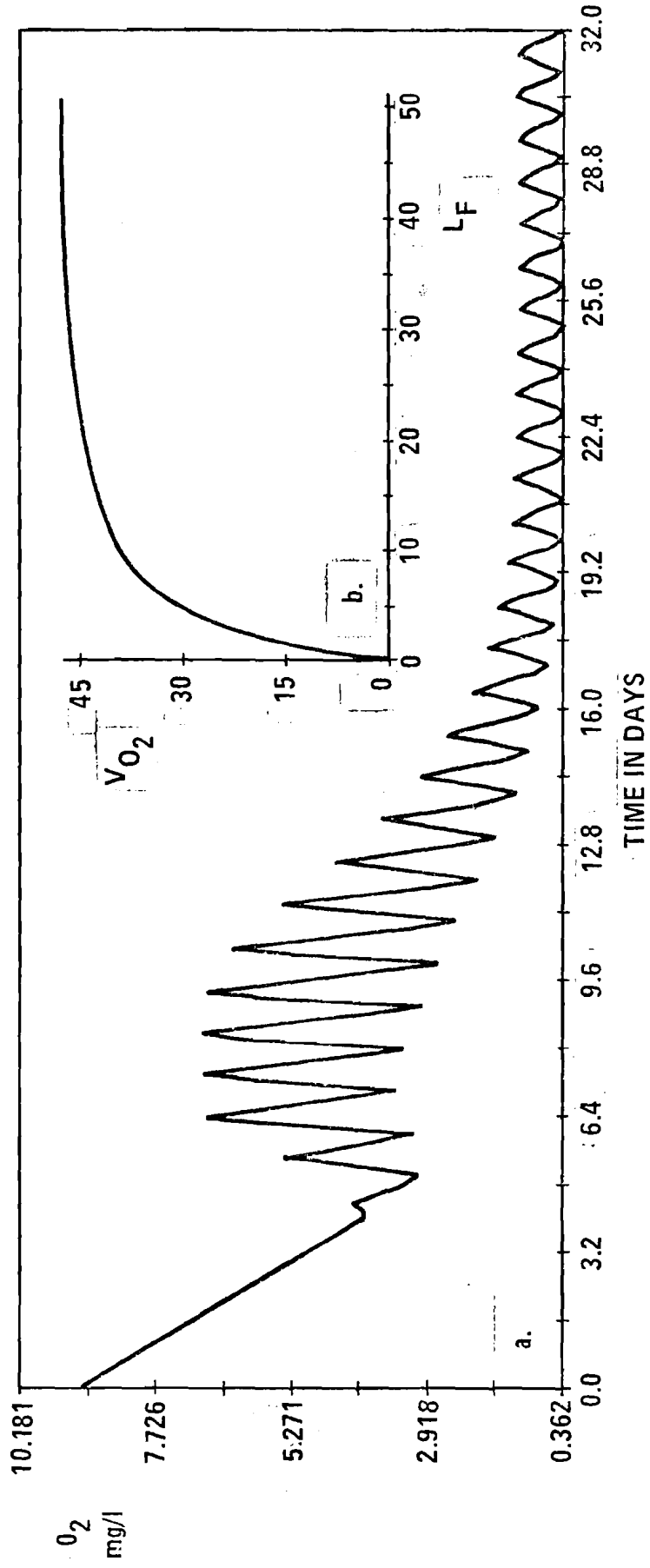


Figure 7. Change of dissolved oxygen content taking into account photosynthetic production. Dependence of specific rate of oxygen production versus excretion of nitrogenous matter is shown in insertion.

Plankton biomasses were assumed to be equal to zero at $t = 0$. In the inflow water only fixed and low values of biomasses were assumed (Table 9). Under such conditions organisms begin to develop after an adaptive period. Phytoplankton adapt in three days, after which they begin to increase their biomass actively during the next four days. Phytoplankton attain a maximum biomass value between the 8th and 11th days. During the same period, biomass fluctuations are observed. These fluctuations are connected with the changes of light intensity. At that time the largest amplitude in the fluctuation of ammonium concentration, as the product of phytoplankton activity, were observed.

By the 16th day phytoplankton concentration decreases approximately by five times (in comparison with the 8th and 11th days), and the steady-state level of biomass is established from the 16th to the 20th day, with small daily fluctuations resulting from light intensity change. During the first six days, after the adaptive period, zooplankton begin to develop in the system. Their growth becomes most active on the tenth day; therefore, during this period the reduction of phytoplankton concentration is observed. Zooplankton growth rate is gradually decreased and after 25 days its concentration reaches the steady-state level. During this period only small daily fluctuations of zooplankton biomass are observed as a result of the influence of light intensity.

The content of detrital nitrogen fluctuates over a small range. Some increase of detritus is seen between the 7th and 9th days, when phytoplankton biomass reaches its maximum. The nitrogen content in the detritus remains practically unchanged after ten days. Its small fluctuations generally coincide with the change of phytoplankton activity.

The changes of dissolved oxygen content in the system are shown in Figure 7a. In this case the influence of atmosphere re-aeration is not taken into account and the observed oscillations of dissolved oxygen concentrations are the result of photosynthetic phytoplankton activity. For estimating the photosynthetic production of oxygen, the relationship given in

Figure 7b was used. This dependence shows the photosynthetic velocity of oxygen liberation (V_{O_2}) as a function of the specific rate of nitrogenous matter liberation (L_F) by phytoplankton. This dependence is described by equation (38). The values used for the coefficients ($g_{18} = 48$; $g_{19} = 0.3$; Table 8) may be more precisely estimated in special laboratory experiments.

Simulation results show that the oxygen content decreases from 9.18 mg O_2/ℓ to 2.8 mg O_2/ℓ during the first 3 to 4 days, when phytoplankton do not grow. At that time the process of phytoplankton adaptation to environmental conditions takes place. When phytoplankton begin active growth, most variations are observed in the content of the dissolved oxygen, which increases in the daytime with photosynthetic oxygen production and decreases during darkness through oxygen consumption in the oxidation of nitrogenous matter and for the respiration of organisms. In this case the photosynthetic oxygen production is higher than the oxygen consumption during the daytime.

Thus, it appears that changes in the concentrations of all components depends on the plankton organisms. The transformation activity of phytoplankton is higher than that of zooplankton. However, the presence of zooplankton has a stimulative effect on phytoplankton activity. Their biomass is maintained at a comparatively low level in the state of potential growth. In other words, the phytoplankton population is maintained in a state of so-called "logarithmic growth", when the organisms are most active.

The content of ammonium is greatest in the inflow water in comparison with the concentration of other mineral nitrogen compounds. Ammonium concentration is also maintained by a comparatively high content of dissolved organic nitrogen which transforms to ammonium. After approximately 15 days, all compound concentrations become evenly balanced, which is due to the following factors: (1) the rate of the inflow water; (2) ratios between chemical compounds in the experimental system and the inflow water; (3) plankton concentrations and their activities; and (4) temperature and light intensity.

Alteration of at least one of the above factors will change the equilibrium and establish new steady-state concentrations in correspondence with the new conditions. Therefore, the results of this previous run for Model 1 show that it is possible, in principle, to use it for studying ecological processes in batch and chemostat experimental systems; the influence of environmental factors on plankton activities and rates of chemical transformations of nitrogenous matter are included. A special study must be conducted to analyze the model sensitivity to changes of values for the preference coefficients. The idea of normalized values of the preference coefficients* for all food sources, using the hypothesis that $\sum d_i = 1$, would require a special study of model structure.

Generally speaking Model 1 can be used for studying the transformation processes of nitrogenous compounds under natural conditions. For this purpose, it would be necessary to make some additions to the model in order to account for hydrodynamical situations and those other environmental factors which are especially significant for a given water body.

5. DESCRIPTION OF MODEL 2

It is evident from the previous discussion on the theoretical aspects of nitrogen transformation, that autotrophic and heterotrophic bacteria are important elements for the conversion and cycling of nitrogen in a water environment. Model 2, in comparison to Model 1, includes the biomasses of three types of bacteria responsible for nitrogen transformation, Nitrosomonas (B_1), Nitrobacter (B_2), and heterotrophs (B_3). It also consists of two groups of plankton organisms (PL1 and PL2), dissolved organic nitrogen (DON), ammonium (NH_4), nitrite (NO_2), nitrate (NO_3), nitrogenous detritus (N_D) and oxygen (O_2) as well as Model 1.

The complete scheme of nitrogen transformation, which represents the relationships between microorganisms and chemical compounds, has already been discussed.

* K. Fedra (IIASA), personal communication

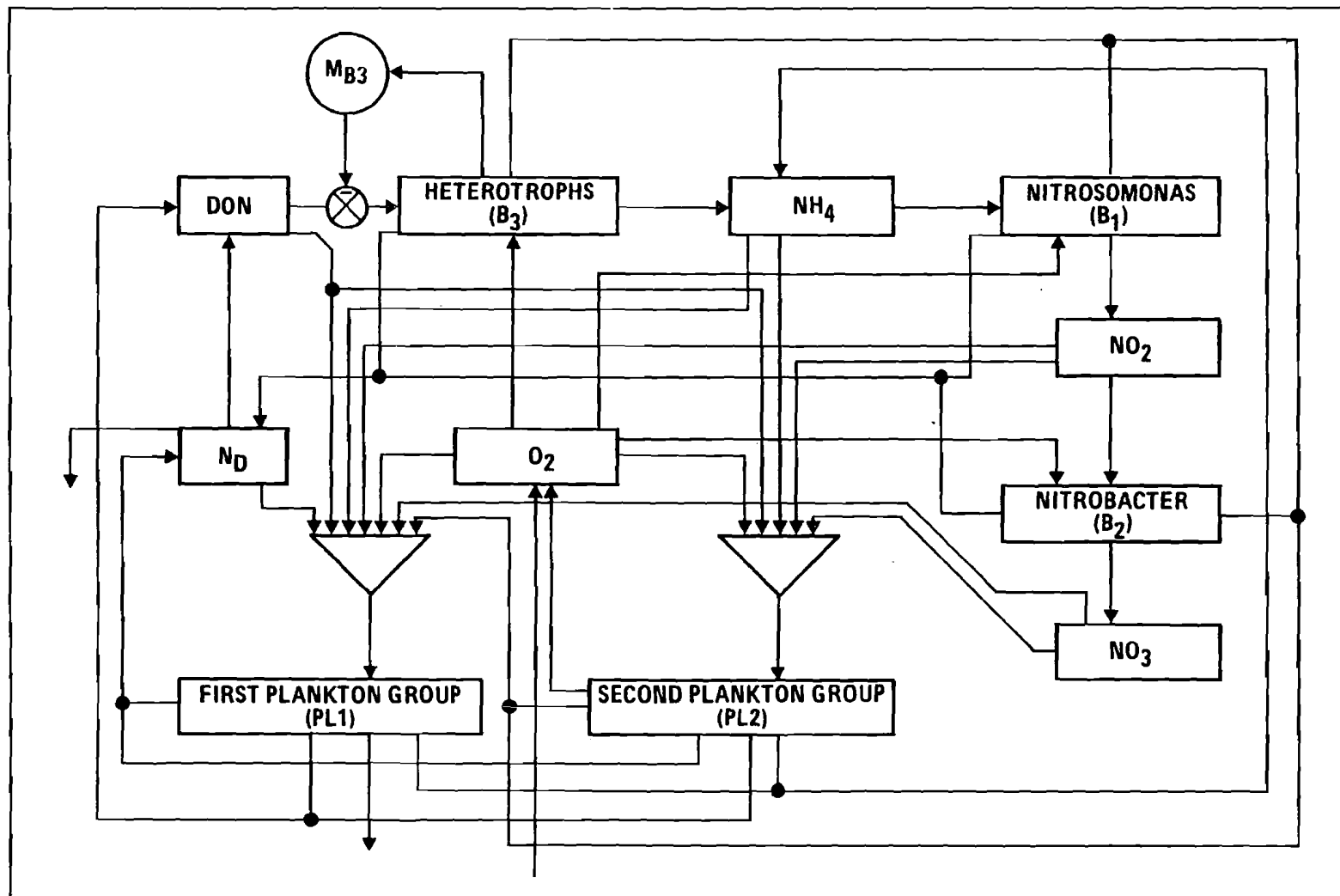


Figure 8. The block-scheme of the compound associations for Model 2.

This scheme is shown in Figure 8. These relationships have been considered in Model 2 to form a complex interacting system that simulates nitrogen transformations under laboratory conditions such as chemostat and batch systems. The parameter V defines the volume of this system and parameter Q defines the rate of inflow of water (for a chemostat system). A description of the individual equations of Model 2 is presented below.

In the given model, microorganism dynamics are described by the following equations:

$$\frac{dPL1}{dt} = (UP_1 - L_1 - S_1) \cdot PL1 - K_7 \cdot PL1 - (Q/V) \cdot (PL1 - PL1^0) \quad (39)$$

$$\frac{dPL2}{dt} = (UP_2 - L_2 - S_2) \cdot PL2 - P_{1PL2} \cdot PL1 - (Q/V) \cdot (PL2 - PL2^0) \quad (40)$$

$$\frac{dB_1}{dt} = (UP_{B1} - L_{B1} - S_{B1}) \cdot B_1 - P_{1B1} \cdot PL1 - (Q/V) \cdot (B_1 - B_1^0) \quad (41)$$

$$\frac{dB_2}{dt} = (UP_{B2} - L_{B2} - S_{B2}) \cdot B_2 - P_{1B2} \cdot PL1 - (Q/V) \cdot (B_2 - B_2^0) \quad (42)$$

$$\frac{dB_3}{dt} = (UP_{B3} - L_{B3} - S_{B3}) \cdot B_3 - P_{1B3} \cdot PL1 - (Q/V) \cdot (B_3 - B_3^0) \quad (43)$$

where

UP_1 , UP_2 , UP_{B1} , UP_{B2} , UP_{B3} are the total specific uptake rates of nitrogen compounds by plankton organisms from the first and second groups, and by Nitrosomonas, Nitrobacter and heterotrophs, respectively (all day^{-1});

L_1 , L_2 , L_{B1} , L_{B2} , L_{B3} are the specific rates of metabolic excretion of the same microorganisms (day^{-1});

S_1 , S_2 , S_{B1} , S_{B2} , S_{B3} are specific non-predation mortality rates of the same microorganisms (day^{-1});

K_7 is rate constant for grazing of the first group of plankton organisms by higher trophic organisms (day^{-1});

P_{1PL2} , P_{1B1} , P_{1B2} , P_{1B3} are specific rates of grazing of plankton of the second group, Nitrosomonas, Nitrobacter and heterotrophs respectively, by the first plankton group (day^{-1});

PL_1^O , PL_2^O , B_1^O , B_2^O , B_3^O are microorganism concentrations in the inflow water for a chemostat system (mgN/l).

The same structure of equations are used here, as in Model 1, for the description of specific rates of uptake, excretion and mortality of plankton organisms, and therefore they will be discussed in this chapter very briefly.

The total specific uptake rates of nutrients by plankton organisms from the first and second groups are described by equations (5) and (6), respectively. In comparison with Model 1 the nitrogen pool for the first plankton group (PoolN_1) includes a larger number of nitrogen sources and is given by

$$\begin{aligned} \text{PoolN}_1 = & d_1 \cdot B_1 + d_2 \cdot B_2 + d_3 \cdot B_3 + d_4 \cdot PL_2 + d_5 \cdot N_D + d_6 \cdot NH_4 \\ & + d_7 \cdot NO_2 + d_8 \cdot NO_3 + d_9 \cdot DON \end{aligned} \quad (44)$$

where d_i are preference coefficients.

The nitrogen pool for the second plankton group* (PoolN_2) includes the same nitrogen sources as in Model 1:

$$\text{PoolN}_2 = d_{10} \cdot NH_4 + d_{11} \cdot NO_2 + d_{12} \cdot NO_3 + d_{13} \cdot DON \quad (45)$$

Uptake of each nitrogen source by plankton organisms from the first and second groups may be expressed by the general equations**:

* It is assumed that the second group is phytoplankton

** K_1 , K_2 , R_{TZ} , R_{TF} , R_{IZ} , R_{IF} coefficients are the same in Models 1 and 2.

for the first plankton group

$$P_{1N} = \frac{K_1 \cdot R_{TZ} \cdot R_{IZ} \cdot d_i \cdot N}{PoolN_1 + PL1} \quad (46)$$

where i for d is changed from 1 to 9 when N = B₁ , B₂ , B₃ , PL2 , N_D , NH₄ , NO₂ , NO₃ , DON , respectively;

for the second plankton group

$$P_{2N} = \frac{K_2 \cdot R_{TF} \cdot R_{IF} \cdot d_i \cdot N}{PoolN_2 + PL2} \quad (47)$$

where i for d is changed from 10 to 13 when N = NH₄ , NO₂ , NO₃ , DON, respectively.

Uptake of nutrients by plankton organisms is determined by temperature and light. Model 2 includes the same equation as Model 1* for the description of reduction coefficients for temperature and light dependence of plankton growth.

The kinetics of substrate uptake by bacteria is described in Model 2 by the Longmuir-Hinshelwood equations (Ajzatullin, 1974):

for Nitrosomonas

$$UP_{B1} = \frac{K_3 \cdot R_{TB1} \cdot NH_4}{1 + G_1 \cdot NH_4} \quad (48)$$

for Nitrobacter

$$UP_{B2} = \frac{K_4 \cdot R_{TB2} \cdot NO_2}{1 + G_2 \cdot NO_2} \quad (49)$$

for heterotrophs

$$UP_{B3} = \frac{K_5 \cdot R_{TB3} \cdot DON}{(1 + G_3 \cdot DON) (1 + G_{18} \cdot M_{B3})} \quad (50)$$

where K₃, K₄ and K₅ are rate constants for the uptake of nutrients by Nitrosomonas, Nitrobacter and heterotrophs

* See equations (19)-(22) and Tables 2 and 3.

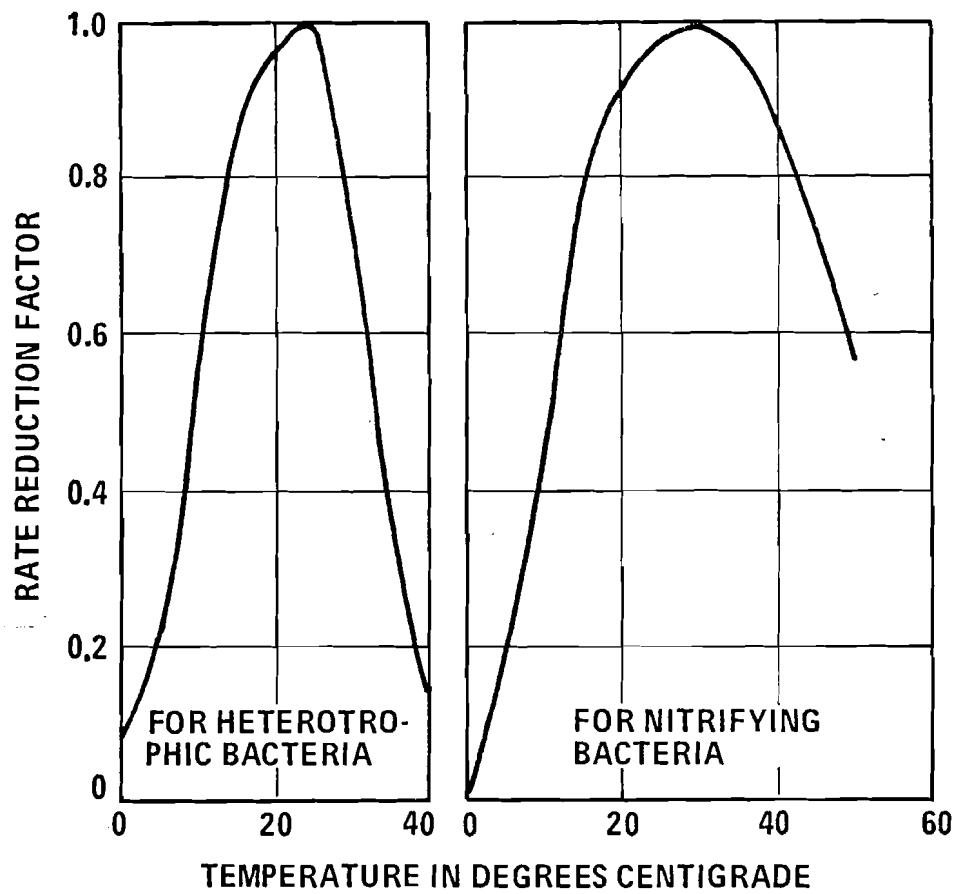


Figure 9. Uptake rate reduction with temperature for bacteria.

$[(\text{mgN}/\ell)^{-1} \text{day}^{-1}]$; G_1 , G_2 and G_3 are constants, the dimensions of which are $(\text{mg}/\ell)^{-1}$. The uptake of nutrients by bacteria is regulated by temperature and the values of the K_3 , K_4 and K_5 coefficients are corrected by reducing coefficients R_{TB1} , R_{TB2} and R_{TB3} , which describe the dependence on temperature for the same bacteria. Heterotrophic bacteria are most active at 22°C - 25°C (Leonov, 1975), while nitrifying bacteria are most active at 30°C (Borchardt, 1966; Wild et al, 1971). These data were used for temperature correction of the uptake-rate constants for bacteria and the curves for temperature dependence are presented in Figure 9. They are described by

$$R_{\text{TB1}} = R_{\text{TB2}} = \frac{0.0759(e^{0.247T} - 1)}{1 + 0.0759e^{0.247T}} - \frac{1.202 \cdot 10^{-5}(e^{0.232T} - 1)}{1 + 1.202 \cdot 10^{-5}e^{0.232T}} \quad (51)$$

$$R_{\text{TB3}} = 0.08 + \frac{0.0316(e^{0.326T} - 1)}{1 + 0.0343e^{0.326T}} - \frac{3.39 \cdot 10^{-5}(e^{0.304T} - 1)}{1 + 3.39 \cdot 10^{-5}e^{0.304T}} \quad (52)$$

Equation (50) takes into account the decreasing specific rate of heterotrophic uptake of DON by inhibitory metabolites which are important for a closed experimental system (Ierusalimsky, 1963). In this equation M_{B3} is the concentration of inhibitory metabolite (mg/ℓ) and G_{18} is an inhibitory constant $(\text{mg}/\ell)^{-1}$.

The specific rates of excretion of plankton organisms are described in Model 2 by equations (23) and (24). For bacteria, these characteristics are presented by an equation in the general form:

$$L_{\text{Bi}} = r_{\text{Bi}} \cdot UP_{\text{Bi}} \quad (53)$$

where $i = 1, 2, 3$ for Nitrosomonas, Nitrobacter and heterotrophs, respectively.

Excretion activity for plankton organisms from the first and second groups are given by equations (25) and (26). For bacteria, this is written as follows

$$r_{Bi} = \frac{a_{4+i} \cdot UP_{Bi}}{1 + a_{5+i} \cdot UP_{Bi}} + \left(1 - \frac{a_{4+i}}{a_{5+i}}\right)$$

where $i = 1, 2, 3$ for Nitrosomonas, Nitrobacter and heterotrophs. a_i has the dimensions (day).

The specific rates of non-predation mortality of all micro-organism species included in Model 2 are described by

for the first plankton group $S_1 = G_4 + G_5 \cdot r_1$ (55)

for the second plankton group $S_2 = G_6 + G_7 \cdot r_2$ (56)

for Nitrosomonas $S_{B1} = G_8 + G_9 \cdot r_{B1}$ (57)

for Nitrobacter $S_{B2} = G_{10} + G_{11} \cdot r_{B2}$ (58)

for heterotrophs $S_{B3} = G_{12} + G_{13} \cdot r_{B3} + G_{14} \cdot M_{B3}$ (59)

where $G_4 - G_{13}$ are constants which have the dimensions day^{-1} ; and G_{14} has dimensions $[(\text{mg}/\ell)^{-1} \cdot \text{day}^{-1}]$.

Equations (55)-(59) account for the fact that under steady-state conditions the specific mortality rate of each micro-organism does not change in practice. A change in the conditions under which microorganisms exist may cause a change in their specific mortality rates. The influence of environmental factors is accounted for by introducing additional terms which show the dependence of the mortality rates of microorganisms on excretion activity and for heterotrophic bacteria on the metabolic inhibitory product (M_{B3}). The ecological significance of metabolites excreted into the water environment by growing microorganisms has been discussed in detail by Lucas (1964).

Inhibitory metabolites are especially important for studying the transformations caused by bacteria in closed (or batch) systems (Ierusalimsky, 1963). Some principal questions for using such schemes for describing the dynamics of heterotrophic bacteria have been discussed by Ajzatullin and Leonov (1975b). The same scheme of metabolite influence on microorganism mortality may be used for any type of microorganisms when there is a necessity for taking this phenomena into account in a simulation of the dynamics of certain microorganism groups in closed systems.

Thus the metabolic inhibitory product (M_{B3}) for heterotrophic bacteria is not identified here and it is introduced in Model 2 as a formal parameter to make this model more flexible for the simulation of nitrogen transformations in experimental systems and batch systems, in particular. Changes in the concentration of M_{B3} are given by

$$\frac{dM_{B3}}{dt} = q_{10} \cdot L_{B3} \cdot B_3 - K_8 \cdot M_{B3} - (Q/V) \cdot (M_{B3} - M_{B3}^O) \quad (60)$$

where q_{10} is the portion of metabolite excreted by heterotrophs (a dimensionless parameter); K_8 is the rate constant for decomposition of M_{B3} (day^{-1}); M_{B3}^O is the content of metabolite in mgN/ℓ in the inflow water for the chemostat system.

It is assumed that the fraction of excreted metabolite, which acts as an inhibitor of heterotrophs, is very small in comparison to other metabolic products, that is organic and mineral nitrogen compounds. For open systems using inhibitory metabolites in a kinetic scheme is obviously unreasonable. In this case, this term can be neglected and its value must be equal to zero.

Biochemical substances appear as a result of the decay of microorganisms and particulate fragments identified as organisms remain. These particulate components are usually called detritus. The change of nitrogenous detritus is described here by the following equation

$$\begin{aligned} \frac{dN_D}{dt} = & q_1 \cdot S_1 \cdot PL1 + q_2 \cdot S_2 \cdot PL2 + q_3 \cdot S_{B1} \cdot B_1 + q_4 \cdot S_{B2} \cdot B_2 + q_5 \cdot S_{B3} \cdot B_3 \\ & - P_{1N_D} \cdot PL1 - K_6 \cdot N_D - K_9 \cdot N_D - (Q/V) \cdot (N_D - N_D^O) \end{aligned} \quad (61)$$

where q_1 - q_5 are dimensionless coefficients; K_6 is a rate constant of direct transformation of detritus to DON (day^{-1}); K_9 is a rate constant for the sedimentation of detritus (day^{-1}); N_D^O is the content of detritus (mgN/ℓ) in inflow water for the chemostat system.

The dynamics of nitrogen compounds are given in Model 2 by the following equations

$$\begin{aligned} \frac{dDON}{dt} = & K_6 \cdot N_D + q_6 \cdot L_2 \cdot PL2 + q_{18} \cdot L_1 \cdot PL1 + (1 - q_7) \cdot L_{B1} \cdot B_1 \\ & + (1 - q_8) \cdot L_{B2} \cdot B_2 + (1 - q_3 - q_{10}) \cdot L_{B3} \cdot B_3 + q_{26} \cdot L_F \cdot PL2 \\ & - P_{1DON} \cdot PL1 - P_{2DON} \cdot PL2 - UP_{B3} \cdot B_3 - (Q/V) \cdot (DON - DON^O) \end{aligned} \quad (62)$$

$$\begin{aligned} \frac{dNH_4}{dt} = & q_9 \cdot L_{B3} \cdot B_3 + (1 - q_6) \cdot L_2 \cdot PL2 + (1 - q_{18}) \cdot L_1 \cdot PL1 - UP_{B1} \cdot B_1 \\ & - P_{1NH_4} \cdot PL1 - P_{2NH_4} \cdot PL2 - (Q/V) \cdot (NH_4 - NH_4^O) \end{aligned} \quad (63)$$

$$\begin{aligned} \frac{dNO_2}{dt} = & q_7 \cdot L_{B1} \cdot B_1 - UP_{B2} \cdot B_2 - P_{1NO_2} \cdot PL1 - P_{2NO_2} \cdot PL2 \\ & - (Q/V) \cdot (NO_2 - NO_2^O) \end{aligned} \quad (64)$$

$$\begin{aligned} \frac{dNO_3}{dt} = & q_8 \cdot L_{B2} \cdot B_2 - P_{1NO_3} \cdot PL1 - P_{2NO_3} \cdot PL2 - (Q/V) \cdot (NO_3 - NO_3^O) \end{aligned} \quad (65)$$

where q_i are dimensionless coefficients; L_F is the rate of photosynthetic production of DON by the second plankton group (day^{-1}); DON^0 , NH_4^0 , NO_2^0 and NO_3^0 are concentrations of nitrogen compounds (mgN/ℓ) in the inflow water.

Fractions of excretion (q_i) of nitrogen compounds by micro-organisms may obviously change. This depends on the physiological state of the population and on the type of water that is under our investigation. Therefore values of q_i in equations (62)-(65) may be taken to range from 0 to 1.

The temperature correction for the rate constants of individual stages of nitrogen transformation is included in this model. The description of temperature corrections for the rate constants $K_1 - K_5$ was considered previously. The rate constant for detritus transformation to DON (K_6) is dependent on temperature (Najarian, Harleman, 1975):

$$K_6 = K_6(0^\circ\text{C}) \cdot T \quad (66)$$

where $K_6(0^\circ\text{C})$ is the value for this constant at 0°C ; T is water temperature in $^\circ\text{C}$.

The dependence on temperature of K_8 and K_9 is given by the general equation

$$K_{8,9} = K_{8,9}(20^\circ\text{C}) \cdot G_{15}^{(T-20)} \quad (67)$$

where $K_{8,9}$ are rate constants at $T^\circ\text{C}$; $K_{8,9}(20^\circ\text{C})$ are values for the same constants at 20°C ; G_{15} is the temperature coefficient. The change in temperature of the water is described by equation (37).

An expression for the dynamics of dissolved oxygen is presented here by

$$\begin{aligned} \frac{dO_2}{dt} = & V_{O_2} \cdot PL_2 - q_{11} \cdot q_{12} \cdot L_1 \cdot PL_1 - q_{13} \cdot q_{14} \cdot L_2 \cdot PL_2 - q_{15} \cdot q_{16} \cdot L_{B_3} \cdot B_3 \\ & - q_{17} \cdot q_{18} \cdot L_{B_1} \cdot B_1 - q_{19} \cdot q_{20} \cdot L_{B_2} \cdot B_2 - G_{16} \cdot K_{re} \cdot (O_2 - O_2^{sat}) \\ & - (Q/V) \cdot (O_2 - O_2^{sat}) \end{aligned} \quad (68)$$

where q_{11} , q_{13} , q_{15} , q_{17} , q_{19} and G_{16} are optional coefficients (dimensionless parameters); q_{12} , q_{14} , q_{16} , q_{18} and q_{20} are stoichiometric constants; V_{O_2} is the rate of photosynthetic production of oxygen by phytoplankton ($mgO_2/mgN/day$); K_{re} is the rate of atmospheric re-aeration (day^{-1}); O_2^{sat} is the oxygen saturation concentration (mgO_2/l).

Thus equation (68) takes into account both the increase of oxygen content by photosynthesis and atmospheric re-aeration and the dilution by inflow water for the chemostat system. It also includes plankton respiration and the oxidation of nitrogen compounds. The content of dissolved oxygen at its saturation point is calculated from an empirical relationship with temperature, i.e. by equation (36). The specific rate of photosynthetic production of oxygen by phytoplankton is given by an equation of the same structure as that for Model 1:

$$V_{O_2} = \frac{q_{21} \cdot q_{22} \cdot q_{24} \cdot L_F}{1 + q_{25} \cdot L_F} \quad (69)$$

where q_{21} is an optional parameter; q_{22} is a stoichiometric coefficient (mgO_2/mgN) and q_{24} and q_{25} are dimensionless parameters.

The main factor which affects the rate of re-aeration (K_{re}) is temperature. An empirical relationship between re-aeration rate and temperature (Isaac, Gaudy, 1968) has been used in Model 2

$$K_{re} = G_{17} \cdot 1,05^{(T - 20)} \quad (70)$$

where G_{17} is the rate constant of re-aeration (day^{-1}).

Together with the general estimation of dissolved oxygen content, this model also takes into consideration the oxygen consumption by respiration of the first and second plankton groups; it also accounts for oxidation of organic and mineral nitrogen forms separately. The following five equations describe the dynamics of biochemical oxygen consumption (BOC_i) for each individual process:

$$\begin{array}{l} \text{respiration of the} \\ \text{first plankton group} \end{array} \quad \frac{dBOC_1}{dt} = q_{11} \cdot q_{12} \cdot L_1 \cdot PL1 \quad (71)$$

$$\begin{array}{l} \text{respiration of the} \\ \text{second plankton group} \end{array} \quad \frac{dBOC_2}{dt} = q_{13} \cdot q_{14} \cdot L_2 \cdot PL2 \quad (72)$$

$$\begin{array}{l} \text{oxidation of } NH_4 \end{array} \quad \frac{dBOC_3}{dt} = q_{15} \cdot q_{16} \cdot L_{B1} \cdot B_1 \quad (73)$$

$$\begin{array}{l} \text{oxidation of } NO_2 \end{array} \quad \frac{dBOC_4}{dt} = q_{17} \cdot q_{18} \cdot L_{B2} \cdot B_2 \quad (74)$$

$$\begin{array}{l} \text{oxidation of DON} \end{array} \quad \frac{dBOC_5}{dt} = q_{19} \cdot q_{20} \cdot L_{B3} \cdot B_3 \quad (75)$$

Estimates for the separate rates of oxygen consumption can be useful for analyzing the system's behavior as a whole and for studying the influence of nitrogen compounds on the oxygen regime at any moment of time. By using only integral characteristics, namely total oxygen content in the water, it is difficult to estimate the influence of nitrogen compounds on the oxygen regime, but by using differentiated rates of oxygen consumption, this is fairly easy to accomplish. Total biochemical oxygen consumption is represented by the sum of

$$BOC = BOC_1 + BOC_2 + BOC_3 + BOC_4 + BOC_5 \quad (76)$$

Model 2 also includes calculations of certain summations of the nitrogenous compounds. They can be of special interest in analyzing the results of modeling, for studying the dynamic properties of individual nitrogen substances, and for examining nitrogen balance as a whole. The following summations can be made:

1. total nitrogen content in living matter

$$N_{\text{living}} = PL1 + PL2 + B_1 + B_2 + B_3 \quad (77)$$

2. total particulate nitrogen

$$N_{\text{part}} = N_{\text{living}} + N_D \quad (78)$$

3. total mineral nitrogen

$$N_{\text{min}} = NH_4 + NO_2 + NO_3 \quad (79)$$

4. total dissolved nitrogen

$$N_{\text{sol}} = N_{\text{min}} + DON \quad (80)$$

5. total nitrogen of the whole system

$$N = N_{\text{part}} + N_{\text{sol}} \quad (81)$$

Model 2 contains in all 76 constants and includes 11 initial concentration values for the five types of microorganisms (bacteria and plankton) and for six chemical compounds. Table 10 includes all the constants used in Model 2, classified in accordance with their functions. Model 2 was constructed in such a way that it was possible to study the influence of the main environmental factors on water quality. If necessary, this model can be easily simplified by removing certain pathways of transformation without disturbing the total scheme of interactions between the compounds considered. For this purpose it is necessary to make the respective values of the optional parameters equal to zero. Variations in metabolic excretions of micro-

Table 10. Main functions for constants in Model 2.

Parameters for description of	Preference coefficients	Coefficients of physiological activity for organisms	Stoichiometric constants for calculations of oxygen consumption and oxygen production	Optional constants
<p><u>Substrate Consumption</u></p> <p>K_1-by First plankton group K_2-by Second plankton group K_3, G_1 -by Nitrosomonas K_4, G_2 -by Nitrobacter K_5, G_3, G_{18}-by Heterotrophs</p> <p><u>Chemical-Ecological Processes</u></p> <p>K_6 — $N_D \rightarrow$ DON K_7 — grazing PL1 K_8 — metabolite decomposition</p> <p>K_9-sedimentation of N_D</p> <p><u>Physical Processes</u></p> <p>G_{15}-temperature coefficient G_{17}-re-aeration</p>	<p><u>For First plankton group</u></p> <p>d_1-grazing of B_1 d_2-grazing of B_2 d_3-grazing of B_3 d_4-grazing of PL2 d_5-utilization of N_D d_6-consumption of NH_4 d_7-consumption of NO_2 d_8-consumption of NO_3 d_9-consumption of DON</p> <p><u>For Second plankton group</u></p> <p>d_{10}-consumption of NH_4 d_{11}-consumption of NO_2 d_{12}-consumption of NO_3 d_{13}-consumption of DON</p>	<p><u>For First plankton group</u></p> <p>a_1, a_2 } excretion of metabolic products q_{23} } G_4, G_5 - mortality</p> <p><u>For Second plankton group</u></p> <p>a_3, a_4 } excretion of metabolic products q_6 } G_6, G_7 - mortality q_{24}, q_{25} - photosynthetic production of oxygen and organic matter</p> <p><u>For Nitrosomonas</u></p> <p>a_5, a_6 } excretion of metabolic products q_7 } G_8, G_9 - mortality</p> <p><u>For Nitrobacter</u></p> <p>a_7, a_8 } excretion of metabolic products q_8 } G_{10}, G_{11} - mortality</p> <p><u>For Heterotrophs</u></p> <p>a_9, a_{10} } excretion of metabolic products q_9 } G_{12}, G_{13}, G_{14} - mortality</p>	<p>q_{12}, q_{14}-plankton respiration q_{16}-oxidation of DON q_{18}-oxidation of NH_4 q_{20}-oxidation of NO_2 q_{22}-oxygen production</p>	<p>q_1 q_2 q_3 q_4 q_5 q_{11} q_{13} q_{15} q_{17} q_{19} q_{21} q_{26} G_{16}</p>

organisms make Model 2 more flexible and thus it may be used for solving different, purely chemical, as well as biological, problems of water quality analysis.

6. SIMULATION

For studying the application of Model 2, different published sources were used to select experimental data in nitrogen transformation studies. However, we failed to find any reports which have data on variations in all the nitrogen compound concentrations, including soluble and suspended substances. This lack of available experimental data limits, to a great extent, the possibilities for correcting estimates of the model constants. Therefore, as much experimental data as possible has been used, especially that which was obtained in laboratory experiments with different types of water samples and where the dynamics of at least the main chemical compounds had been studied. Comparatively wide-ranging experimental data were obtained in tests conducted with sewage (De Marco et al, 1967), river (Knowles et al, 1965), sea (Brand, Rakestraw, 1941) and lake waters (Votintsev, 1948). All these experiments were performed at laboratory temperatures of 18^o-20^oC and in darkness. Thus, photosynthetic production of organic matter and oxygen by plankton is not taken into account in these applications of the model. All tests were carried out in batch systems and for all further cases considered the parameter Q equals zero.

6.1 Simulation of Nitrogen Transformation in Sewage and River Waters

Experiments with sewage (De Marco et al, 1967) and river water (Knowles et al, 1965) were conducted with a higher initial concentration of ammonium compared to concentration dissolved organic nitrogen. This means that experiments began when DON transformation to ammonium* had been already completed or was close to completion. After completion of the ammonification stage, the DON content does not change much and these alterations

* stage of ammonification

should not significantly influence the development of subsequent stages of nitrogen transformation, namely ammonium to nitrite and nitrite to nitrate^{**}.

De Marco et al (1967) have presented the most detailed experimental data on nitrogen transformations in sewage. They measured experimentally the content of DON, NH_4 , NO_2 and NO_3 . Figure 10 compares the results of the model (curves) with the experimental data (points) of De Marco et al (1967). The input parameters of Table 11 allow a sufficiently accurate picture of nitrogen transformation in sewage. DON concentration changes slowly in the system and this indicates an insufficient activity of heterotrophs during the whole period of the experiment, in spite of the high content of DON in the system. Traditional methods of modeling, using Michaelis-Menten and Monod expressions are not sufficient for a description of feedback in DON consumption by heterotrophs. Introducing a kinetic scheme with inhibition products of bacteria (M_{B3}), and their negative feedback on bacterial development, significantly increases the simulation possibilities of Model 2.

For describing metabolite influences on the growth of heterotrophs comparatively low initial concentrations $M_{B3} = 0.2 \text{ mgN}/\ell$ with a high rate of metabolite decomposition, $K_8 = 0.4 \text{ day}^{-1}$, were used. An inhibitory influence of the metabolite on the specific rate of heterotroph mortality, $G_{14} = 75$, as well as on DON utilization, $G_{18} = 700$, was also taken into account (Table 11). In this case metabolites should be considered as formal parameters and as an index of media and population states.

The slow decrease of DON in time generally indicates unfavorable conditions in the system for the functioning of the heterotrophs since, as is known from the Michaelis constant, less than $0.5 \text{ mgN}/\ell$ of DON is required for their active growth (Harleman, 1978).

** stage of nitrification

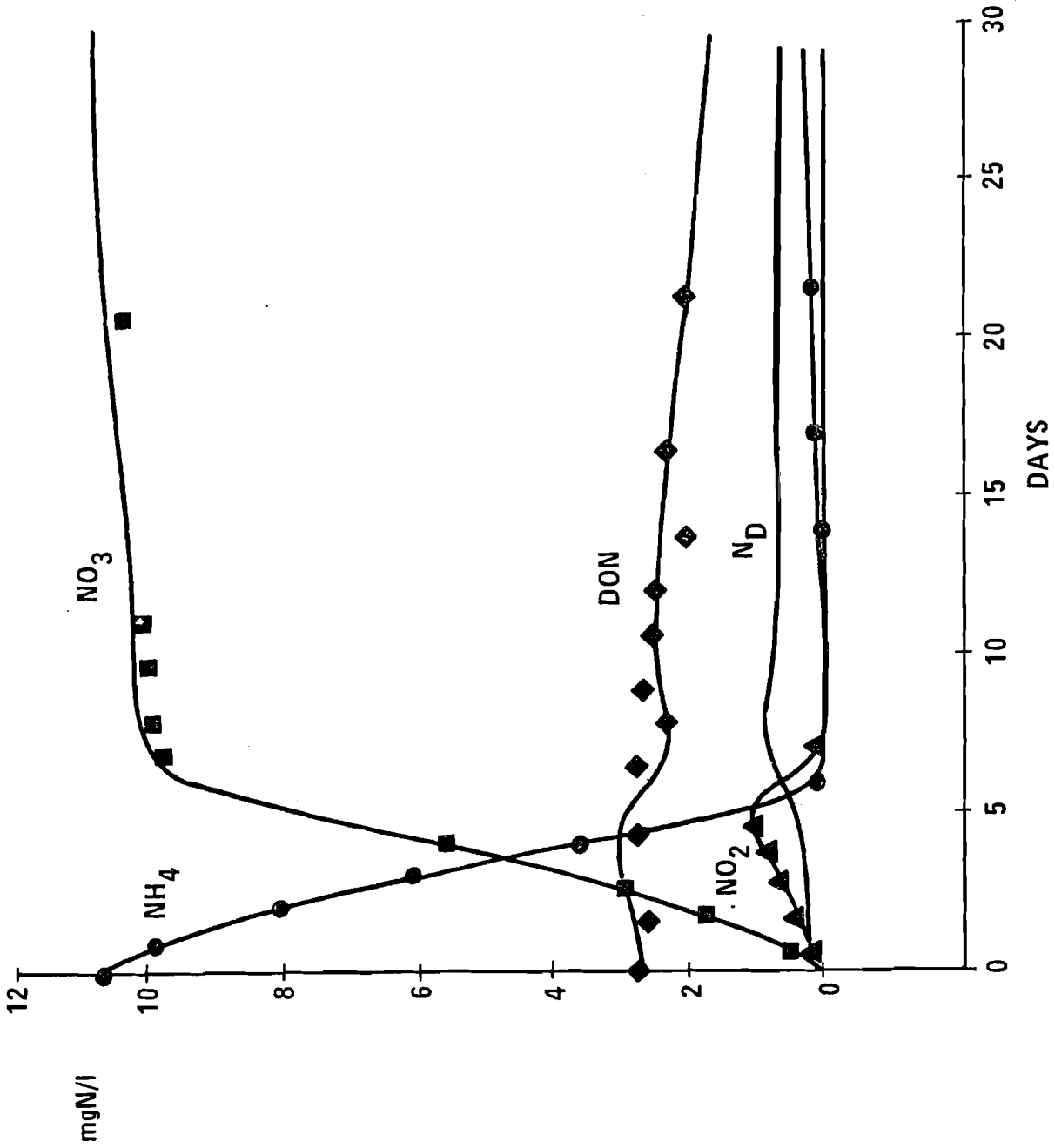


Figure 10. Comparison of simulation results (curves) with experimental data (points) of De Marco et al (1967), Model 2, sewage water, input parameters in Table 11.

Table 11. Initial concentrations of nitrogenous compounds for sewage and values of rate constants used in modeling (for Figure 10).

Nitrogen compounds	Values	Parameters	Values	Parameters	Values	Parameters	Values
DON	2.7	K_{1-2}	-	G_1	0.5	q_{1-2}	-
NH_4	10.8	K_3	11.0	G_2	0.5	q_3	1.0
NO_2	0	K_4	12.0	G_3	5.0	q_4	1.0
NO_3	0	K_5	105.6	G_{4-7}	-	q_5	1.0
N_D	0.1	K_6	0.025	G_8	0.1	q_6	-
B_1	0.065	K_7	-	G_9	0.05	q_7	1.0
B_2	0.5	K_8	0.4	G_{10}	0.3	q_8	1.0
B_3	0.04	K_9	0.0	G_{11}	0.1	q_9	0.97
PL1	0	d_{1-13}	-	G_{12}	0.8	q_{10-14}	-
PL2	0	a_{1-4}	-	G_{13}	0.4	q_{15}	1.0
M_{B3}	0.02	a_5	1.5	G_{14}	75.0	q_{16}	13.35
		a_6	1.875	G_{15}	1.05	q_{17}	1.0
		a_7	2.1	G_{16}	1.0	q_{18}	3.42
		a_8	2.62	G_{17}	1.25	q_{19}	1.0
		a_9	0.0085	G_{18}	700.0	q_{20}	1.14
		a_{10}	0.0121			q_{21-26}	-

Parameters for plankton not listed.

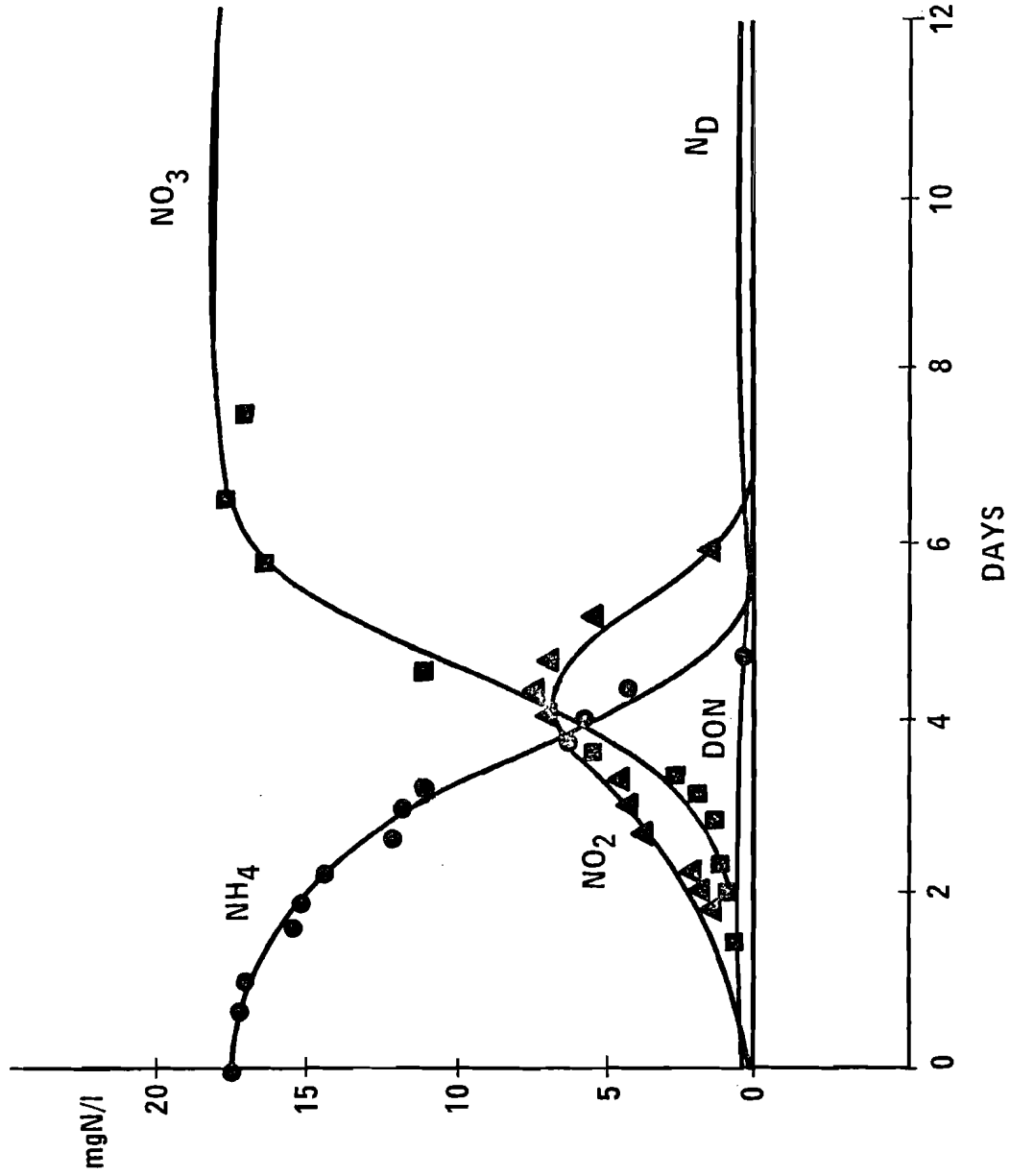


Figure 11. Comparison of simulation results (curves) with experimental data (points) of Knowles et al. (1965) Model 2, river water, in part parameters in table 12

For the given coefficient values it was possible to obtain a relatively accurate picture of the modeling of DON dynamics (Figure 10). This fact can be regarded as indirect evidence for the correctness and sufficiency of the prerequisite conditions for describing heterotrophic functions in closed (batch) systems. In modeling the growth of *Nitrosomonas* and *Nitrobacter* there was no necessity for accounting for the inhibitory influence of metabolites on the development of nitrifying bacteria.

In sewage the ammonium concentration quickly decreases from 10.8 mg/ℓ (at the initial moment of time) to practically zero by the seventh day. Nitrite reaches an intermediate maximum (~1 mg/ℓ) on the fifth day. In this case rapid transformation of a nitrogen compound to the final product, i.e. nitrate, takes 7-8 days in all. However, by this time 93.5% of the initial ammonium has been converted. The remainder is dispersed as suspended materials, i.e. biomass of nitrifying bacteria and partial detritus. Only by the 30th day does the nitrate content become close to the initial amount of ammonium concentration. Thus, by this day nitrification can be regarded as complete.

A similar picture of nitrogen transformations in river water was also observed by Knowles et al (1965). In this case the initial ammonium content was 17.5 mg/ℓ. Figure 11 compares the experimental data obtained by Knowles et al (1965) with the simulation results, represented by curves. Simulation runs were conducted with the input data presented in Table 12. A comparatively low DON concentration (0.5 mg/ℓ) was used, since there were no values for the initial concentration of organic nitrogen (Knowles et al, 1965). In the simulation results, DON content decreases during the first seven days to 0.076 mg/ℓ. After the seventh day it practically does not change its level. However, ammonium content always decreases to zero during 4.5 days. Nitrite reaches its intermediate maximum (~6.5 mg/ℓ) on the 4th day. During the first seven days detritus concentration increases from an initial 0.01 mg/ℓ to 0.22 mg/ℓ and then stays at that level.

In a river water test, complete nitrogen transformation to nitrate takes 5.5 days, which is less than in the experiment

Table 12. Initial concentrations of nitrogen compounds for river water and values of rate constants used in modeling (for Figure 11).

Nitrogen compounds	Values	Para- meters	Values	Para- meters	Values	Para- meters	Values
DON	0.5	K_{1-2}	-	G_1	0.01	q_{1-2}	-
NH_4	17.5	K_3	25.0	G_2	0.01	q_3	1.0
NO_2	0.25	K_4	30.0	G_3	5.0	q_4	1.0
NO_3	0.1	K_5	105.6	G_{4-7}	-	q_5	1.0
N_D	0.01	K_6	0.02	G_8	0.2	q_6	-
B_1	0.0015	K_7	-	G_9	0.0	q_7	1.0
B_2	0.008	K_8	0.4	G_{10}	0.15	q_8	1.0
B_3	0.04	K_9	0.0	G_{11}	0.0	q_9	0.97
PL1	0	d_{1-13}	-	G_{12}	0.2	q_{10-14}	-
PL2	0	a_{1-4}	-	G_{13}	0.4	q_{15}	1.0
M_{B3}	0.02	a_5	0.5	G_{14}	75.0	q_{16}	13.35
		a_6	0.67	G_{15}	1.05	q_{17}	1.0
		a_7	1.0	G_{16}	1.0	q_{18}	3.42
		a_8	1.39	G_{17}	3.0	q_{19}	1.0
		a_9	0.0073	G_{18}	300.0	q_{20}	1.14
		a_{10}	0.0182		-	q_{21-26}	-

Parameters for plankton not listed.

with sewage discussed above. Dynamic transformation of nitrogen, both organic and mineral compounds, is determined by the activity of heterotrophs, Nitrosomonas and Nitrobacter. Distinctions between bacteria functioning under different environmental conditions, i.e. river water and sewage, were brought to light only by considering the rate constants and initial component concentrations (both biological and chemical) considered in these two cases (Tables 11 and 12).

In modeling nitrogen transformations in sewage and river water the same initial concentration of heterotrophic bacteria ($B_3^O = 0.04 \text{ mg}/\ell$) and metabolites ($M_{B_3}^O = 0.02 \text{ mg}/\ell$) were used (Tables 11 and 12). Parameter values for growth rate* and elimination** of heterotrophs and metabolite decontamination ($K_8 = 0.4 \text{ day}^{-1}$) also remained unchanged. Values of natural decay (G_{12}) for heterotrophs in river and sewage water significantly differ from each other and equal 0.2 and 0.8 day^{-1} respectively.

For describing different rates of organic nitrogen consumption by heterotrophs it was necessary to use various values of G_{14} that show the metabolite influence on substrate consumption by heterotrophs (700 and 300 for sewage and river water respectively). Finally, values of the a_9 and a_{10} coefficients were selected to describe heterotroph activity. When we change the values of these coefficients we can shift the biomass organism peak without influencing the rate of substrate uptake and without disturbing the substrate transformations. The ratio of a_9/a_{10} determines the rate of ammonium liberation by heterotrophic bacteria at all stages of population development***. With limited quantities of substrate content the specific rate of ammonium liberation depends on the difference $(1 - a_9/a_{10})$

* Maximum growth rate (K_5) and its limiting coefficient (G_3) for heterotrophs.

** G_{13} and G_{14} show the influence of activity and metabolites to specific rate of heterotroph mortality, respectively.

*** Ammonium liberation as a result of vital functions is most intensive when heterotrophs grow actively.

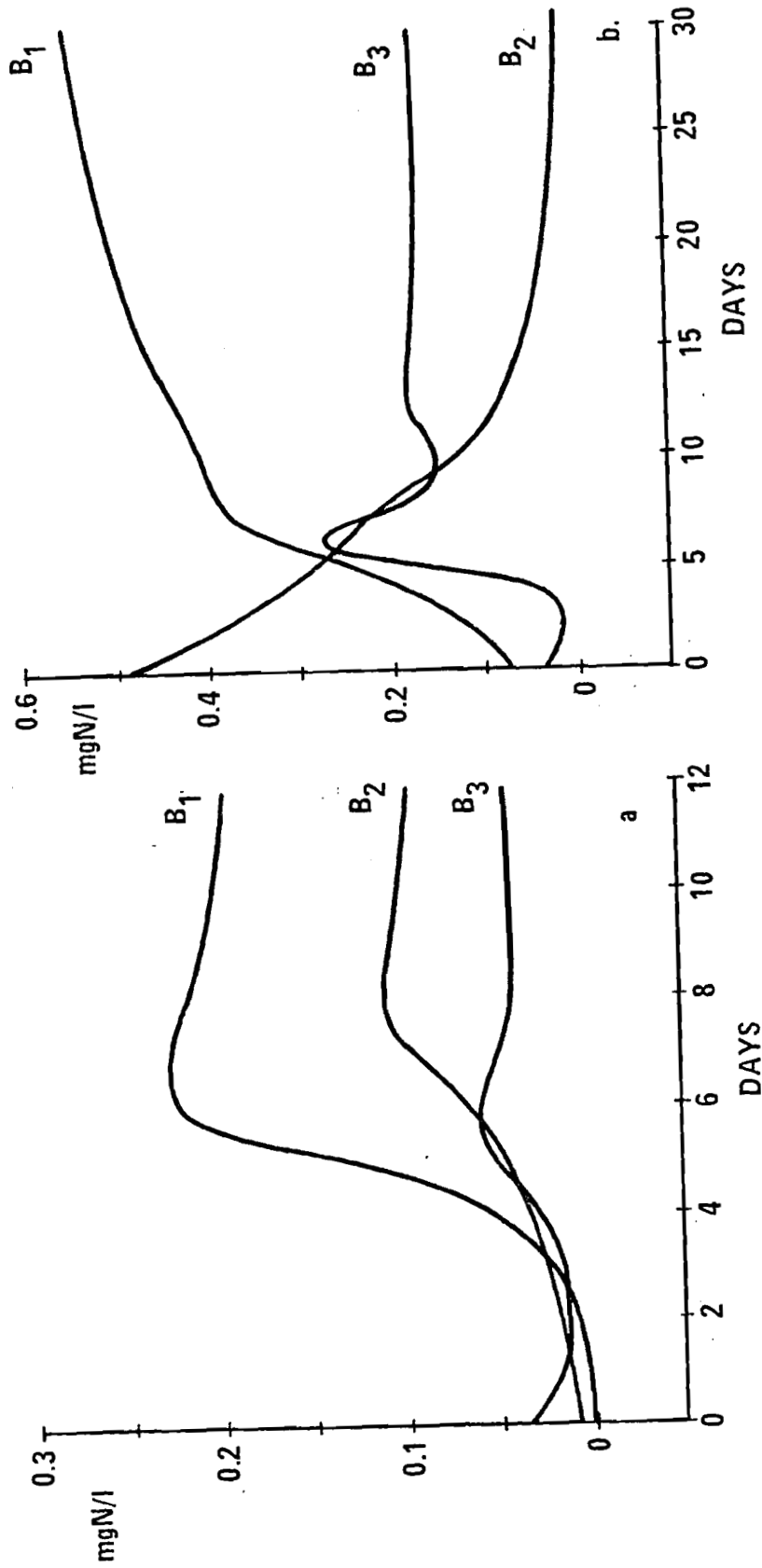


Figure 12. Change of bacteria concentration in the river water (a) and sewage (b).
B₁ - Nitrosomonas; B₂ - Nitrobacter; B₃ - Heterotrophs.

included in equation (54). It should be noted that the selected coefficient values of a_9 and a_{10} (Tables 11 and 12) for experiments with sewage and river water reflect differences in heterotroph activity. The fraction of metabolite liberation equals approximately 30% in sewage and 60% in river water from the total amount of consumed substrate. Out of all the liberated matter 97% consists of ammonium ($q_9 = 0.97$), and only 3% ($q_{10} = 0.03$) is metabolite. Metabolite accumulation in the water decreases the rate of heterotrophs growth.

The curves on Figure 12 show how the biomasses of heterotrophs, Nitrosomonas and Nitrobacter change in river water and sewage for 12 and 30 days, respectively. The growth dynamics for all bacteria significantly differs in either water medium. The average amount of bacterial biomass is higher in sewage (Figure 12b). The low content of organic nitrogen in river water prohibits the active growth of heterotrophs. Simulation results give very smooth curves for heterotrophic biomass growth in river water (Figure 12a). On the contrary, Model 2 gives typical curves for bacterial growth in sewage and reflects a specific stage of population development, including log phase, logarithmic growth phase and dying phase (Schlegel, 1972). The maximum heterotroph concentration of 0.266 mg/l occurred on the sixth day. During the 6-10 day period their biomass decreased to 0.144 mg/l. After approximately the 15th day dynamic equilibrium is established in the water. During this period, the heterotroph steady-state concentration equals 0.164 mg/l. This concentration corresponds to new conditions in the way that the heterotrophs function. The biomass of heterotrophs at this level is four times higher than their initial concentration. Figure 12 also shows curves for the changing biomass of nitrifying bacteria. For describing the Nitrosomonas and Nitrobacter development which would satisfy the experimental pattern of changes in the mineral nitrogen compound concentrations (in sewage and river water), it was necessary to select and change values for the growth coefficients (K_3 and K_4), the limiting coefficient for growth rates (G_1 and G_2) and the parameters used for bacterial decay rates (G_{8-11}).

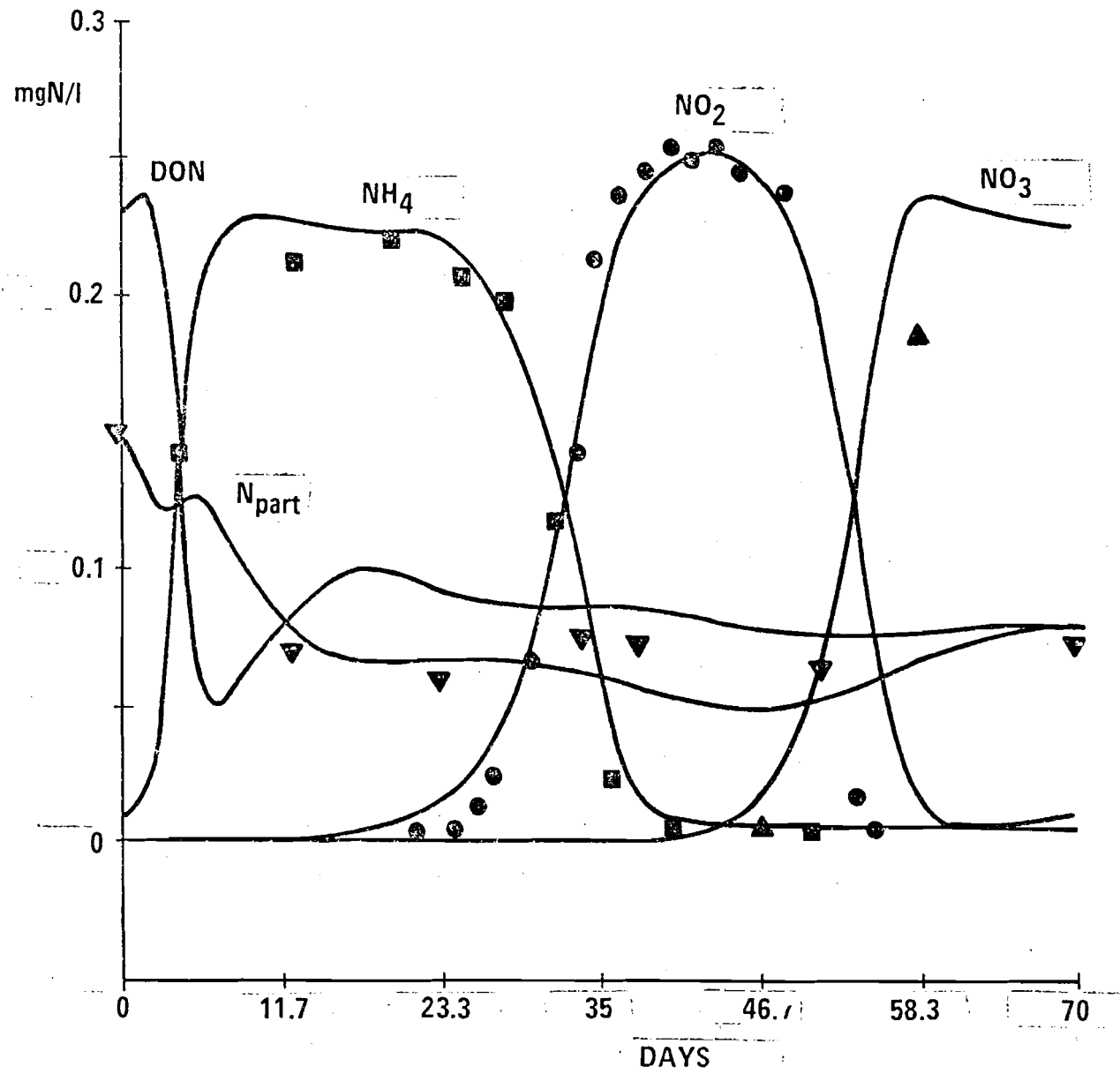


Figure 13. Comparison of simulation results (curves) with experimental data (points) of Brand, Rakestraw (1941).
Model 2.sea water,input parameters in table 13.

Nitrifying bacteria possess very high oxidation abilities (Ruban, 1961). However, these bacteria are considered to be slow-growing organisms (Painter, 1970; Keeney, 1972). These peculiarities in the activities of nitrifying bacteria are reproduced by the ratios between coefficients a_5/a_6 (for Nitrosomonas) and a_7/a_8 (for Nitrobacter) in equation (54). These coefficient values must show comparatively low fractions of nitrogen included in the bacteria cell matter as compared to the total nitrogen involved in metabolism.

At low substrate concentrations, 20-30% of the matter taken up is assimilated by nitrifying bacteria. The fraction of the nitrogen taken up that is excreted by the nitrifying bacteria increases to 95-98% when nitrogenous mineral compounds are in abundance. Mineral nitrogen compounds can be considered as energy sources for nitrifying bacteria if one assumes that their oxidation activity of extra-cellular ferments is as given using suggestion of Ruban (1961).

The above coefficients describe sufficiently the dynamics of organic and mineral nitrogen transformations as observed in tests with sewage and river water. Thus, in this case, by using chemical characteristics, the adequacy of the description for ecological processes has been sufficiently tested.

6.2 Simulation of Nitrogen Transformation in Sea and Lake Water

In tests with sea (Brand, Rakestraw, 1941) and lake (Votintsev, 1948) water, the influence of plankton decomposition in darkness on nitrogen transformation was studied. Autolysis of plankton stimulates the bacterial destruction of nitrogenous compounds, including mainly organic compounds (Golterman, 1964). Changes in the concentrations of ammonium, nitrite, nitrate and the nitrogen in particulate matter were studied in sea water for a 70 day period (Brand, Rakestraw, 1941). Simulation results and experimental data (Brand, Rakestraw, 1941) for sea water experiments are compared in Figure 13. The input data presented in Table 13 were used for the model. The initial ammonium concentration was very low. In the model the dynamics of nitrogen transformation was simulated from the ammonification stage

Table 13. Initial concentrations of nitrogenous compounds for sea water and values of rate constants used in modeling (for Figure 13).

Nitrogen compounds	Values	Parameters	Values	Parameters	Values	Parameters	Values
DON.	0.23	K ₁	-	a ₈	1.83	q ₁	-
NH ₄	0.01	K ₂	70.0	a ₉	0.06	q ₂	1.0
NO ₂	0	K ₃	330.0	a ₁₀	0.15	q ₃	1.0
NO ₃	0	K ₄	300.0	G ₁	15.0	q ₄	1.0
N _D	0.01	K ₅	74.0	G ₂	12.0	q ₅	1.0
B ₁	5·10 ⁻⁷	K ₆	0.015	G ₃	0.5	q ₆	0.0
B ₂	3·10 ⁻⁸	K ₇	-	G ₄₋₅	-	q ₇	1.0
B ₃	1·10 ⁻⁴	K ₈	0.05	G ₆	0.3	q ₈	1.0
PL1	0	K ₉	0.0	G ₇	0.0	q ₉	0.97
PL2	0.14	d ₁₋₉	-	G ₈	0.1	q ₁₀	0.03
M _{B3}	0	d ₁₀	7·10 ⁻⁴	G ₉	0.12	q ₁₁₋₁₂	-
		d ₁₁	3·10 ⁻⁴	G ₁₀	0.05	q ₁₃	1.0
		d ₁₂	5·10 ⁻⁴	G ₁₁	0.1	q ₁₄	13.35
		d ₁₃	0.0	G ₁₂	0.5	q ₁₅	1.0
		a ₁₋₂	-	G ₁₃	0.0	q ₁₆	13.35
		a ₃	0.2	G ₁₄	85.0	q ₁₇	1.0
		a ₄	0.202	G ₁₅	1.05	q ₁₈	3.42
		a ₅	1.7	G ₁₆	1.0	q ₁₉	1.0
		a ₆	1.83	G ₁₇	1.25	q ₂₀	1.14
		a ₇	1.7	G ₁₈	100.0	q ₂₁₋₂₆	-

onwards. The initial concentration of dissolved organic nitrogen was considered to be equal to 0.23 mg/l (Table 13). The nitrogen content of the total initial biomass of decomposable algae was equal to 0.14 mg/l (Brand, Rakestraw, 1941).

According to the nitrogen transformation scheme adopted for this model, plankton decomposition should be accompanied by an increase in detritus during the first few days of the experimental period. Detritus is transformed comparatively quickly to DON. It is also known that the process of phytoplankton death is a comparatively fast one, and complete death of phytoplankton cells can be reported after five days of the experiment. However, during autolysis the liberation of nitrogenous matter proceeds very slowly (Golterman, 1964). According to our simulation results, intensive growth of heterotrophs and rapid ammonium production is observed during phytoplankton decomposition. However, during 3-5 days only about 20-30% of the total amount of ammonium formed appears to be excreted by phytoplankton, while the main part of ammonium that has been formed is a result of the activity of heterotrophs, which transform DON to ammonium (Golterman, 1964). The shape of the curve for DON concentration variations is very similar to the experimental curves of organic matter transformations which have already been published in papers on the subject. Simulation results confirm the fact that not all the organic nitrogen transforms to ammonium. The DON content in the water results from simultaneous processes of nitrogen utilization, decomposition of detritus, and excretion of organisms in the form of metabolic products. According to the simulation results the remaining DON concentration, which is due to the equilibrium of the above-mentioned processes, is 34.8% of its initial concentration. The total remaining concentration* (close to steady-state), is about 40% of the initial concentration of total nitrogen. These values agree with experimental estimates made in laboratory studies on organic matter decomposition in sea water (Skopintsev et al, 1965). The simulation results given in Figure 13 correspond very closely with the quantitative scheme

* Sum of organic nitrogen in soluble and particulate forms.

of nitrogen transformations as observed in experiments and as published elsewhere.

Decomposition of organic material, such as excreta and the remains of plankton and algae, constitutes the basis of nutrient cycling in natural waters. This process is one of the main processes in forming the productivity of mineral cycles (Kleerekoper, 1953).

To judge the degree of plankton decomposition, data on residual concentrations of particulate organic matter, on the accumulation of mineral products or on oxygen consumption are used. In a natural environment, the complete mineralization of organic matter seldom takes place (Skopintsev, 1976). Quantitative and qualitative aspects of plankton decomposition have been studied by many authors and significant experimental data are now available in many published papers. Plankton decomposition has been studied under both aerobic and anaerobic conditions. Tables 14 and 15 give some quantitative data that have been estimated experimentally. As a rule, all these tests were conducted in order to study nitrogen transformations and organic matter mineralization. More detailed information can be found in Skopintsev's report (Skopintsev, 1976).

The degree of plankton mineralization in various water media can change from 20 to 94% (Table 14), though under aerobic conditions this degree is higher (Skopintsev, 1976). The residual nitrogen concentration in particulate matter changes from 5 to 87% (Table 14). During plankton decomposition, a certain portion of the organic and mineral nitrogen is released into the water (Table 15). From the technical point of view experimental studies on plankton mineralization are very difficult (Kleerekoper, 1953). Quantitative estimation of the organic and mineral nitrogen liberated into the water by plankton mineralization may not be very accurate because of the complexity of the biochemical processes of transformation taking place simultaneously.

With Model 2 it is possible to estimate the influence of plankton mineralization on nitrogen transformations. These estimates can be performed by using the experimental data of

Table 14. Extent of plankton decomposition in dark conditions.
(Literature review)

Water	Plankton	T°C, conditions	Extent of Mineralization	Remaining Concentration	References
Fresh	Mixed plankton	-	53-97%	-	Kleerekoper, 1953
Fresh	Zooplankton	18-20°, aerobic	66-72% for 20-30 days	-	Krause, 1959
Fresh	Algae	18-20°, anaerobic	77-87% for 20-30 days	-	
Fresh	Algae	20°, aerobic, sterile	20-30% for 5 days	70-80%	Golterman, 1960
Fresh	Algae	20°, aerobic	45-50% for 5 days		
Sea	Mixed plankton	14°, aerobic	50% for 5 days	5% after 5 days	Golterman, 1964
Fresh	Mixed plankton	14°, anaerobic	70% for 60 days	25-30%	Skopintsev et al, 1965
Fresh	Mixed plankton	20°, anaerobic	55-60% for 60 days	-	
Fresh and sea	Growth for 29-54 days plankton	20°, anaerobic	-	18-33% after 200 days	Foree, McCarty, 1970
Fresh	Mixed plankton	20°, aerobic	-	21-64% after 200 days	
Fresh	Algae	20° and 35°, aerobic	-	12-87%	Jewell, McCarty, 1971
Fresh	Phytoplankton	20°, anaerobic	70-71% for 30-220 days	33-18% for 30-220 days	Otsuki, Hanya, 1972
Fresh	Phytoplankton	20°, aerobic	40-64%		
Fresh	Phytoplankton	20°, aerobic	55-72% for 20 days	-	Kudriavtsev, Romanenko, 1973

Brand, Rakestraw (1941), who measured the nitrogen content in particulate matter. In modeling nitrogen transformations in sea water the content of particulate nitrogen was included in the biomass of all the organisms (heterotrophs, Nitrosomonas, Nitrobacter and phytoplankton) and in the detritus. The model reproduces the experimentally observed pattern of nitrogen transformations in sea water (as shown in Figure 13) with the use of the input data presented in Table 13. These parameters are also used in other simulation runs in which the initial plankton concentration is taken as equal to zero. Changes in the relative nitrogenous compound concentrations as percentages of the initial sum of nitrogen concentration in the sea water are compared in Table 16. Results show that the relative nitrogen content in detritus, organism biomasses and DON are generally higher in the phytoplankton system. Nitrogen content in the detritus and biomass are higher at 8.4% and 7.8% respectively. The DON concentrations, close to those of the steady-state, are established in both systems after the expiration of about 10 days. Their concentrations are always 6.2% higher when phytoplankton are present. At the same time the relative concentration of mineral nitrogen is approximately 18.8% higher without phytoplankton. The ratio of soluble nitrogen content to particulate nitrogen remains on the whole lower in the system with phytoplankton than without (Table 16). However, actual concentrations of all nitrogen forms are higher when phytoplankton are present (Figure 14). Table 17 shows the possibility of estimating the influence of plankton decomposition on compound composition. Plankton decomposition occurs within 10 days. The nitrogen concentration bound to the biomass changes little, namely from 13 to 20% during a 10-70 day period. Residual plankton concentration during that period changes between 10-19%. As the simulation results show total mineralization of plankton constitutes 81-90%. During plankton decomposition for the period of 10-70 days, 26-33% of organic nitrogen and 16-42% of mineral nitrogen are liberated into the water. During this period a significant fraction of nitrogen (16-26%) is present in the detritus.

Table 15. Formation of organic and mineral nitrogen forms during decomposition of plankton and algae (Literature review).

Water	Plankton	T°C, con- ditions	Formation of		References
			organic nitrogen	mineral nitrogen	
Sea	Mixed plankton	16-20°, aerobic	-	50% for 19 days	Waksman et al, 1933
Sea	Mixed plankton	18-20°, aerobic	-	60-78% for 8-10 days	Brand et al, 1937
Fresh	Phyto-plankton	6° and 16°, aerobic	-	60-70% for 17-20 days	Skopintsev, Brook, 1940
Fresh	Zoo-plankton	16°, aerobic	-	94% for 20 days	Votintsev, 1948
Fresh	Phyto-plankton	16°, aerobic	-	95% for 10 days	Votintsev, 1953
Fresh	Zoo-plankton	-	-	20-30% for 5 days	Golterman, 1964
Sea	Seaweeds	-	28% from gross production	-	Khailov, Burlakova, 1969
Fresh	Green algae	20°, an-aerobic	8% for 60 days	48% for 60 days	Otsuki, Hanya, 1972
Sea	Macrophyte	-	30-40%	-	Otsuki, Wetzel, 1974

Thus, quantitative estimates of the influences of plankton decomposition, obtained from the simulation runs, correspond with the available experimental data. The application of the model allows a quantitative explanation of kinetic experimental data and gives a new interpretation for the transformation process. With a purely empirical approach it is very difficult to establish those indexes which reflect the actual intensity of the transformations.

In lake water, the dynamics of ammonium, nitrite and nitrate were experimentally studied during a 50 day period (Votintsev,

Table 16. Change of relative concentrations for nitrogen compounds in percentage of initial sum of nitrogen (N_{sum}) in the system (modeling).

Time in days	$N_{\text{sum}} = 0.39 \text{ mg/l}; F^{\circ} = 0.14 \text{ mg/l}$						$N_{\text{sum}} = 0.25 \text{ mg/l}; F^{\circ} = 0$					
	N_{soluble}		$N_{\text{particulate}}$		N_{soluble}	Mass balance	N_{soluble}		$N_{\text{particulate}}$		N_{soluble}	Mass balance
	DON	N_{mineral}	N_{detritus}	N_{living}	$N_{\text{partic.}}$		DON	N_{mineral}	N_{detritus}	N_{living}	$N_{\text{partic.}}$	
0	59.0	2.6	2.6	35.8	1.6	100	92.0	4.0	4.0	0.04	23.8	100
2	61.0	5.2	13.6	20.2	2.0	100	88.7	8.3	2.5	0.5	32.4	100
4	41.0	28.1	16.2	14.7	2.2	100	52.7	38.9	4.1	4.3	10.9	100
6	14.3	53.0	19.9	12.8	2.1	100	15.1	69.4	10.1	5.4	5.5	100
8	13.5	57.9	19.1	9.5	2.5	100	10.7	76.5	10.6	2.2	6.8	100
10	17.1	58.7	16.1	8.1	3.1	100	12.3	79.0	7.8	0.9	10.5	100
20	25.0	58.5	9.3	7.2	5.0	100	16.6	82.3	0.9	0.2	95.6	100
30	21.9	61.6	9.3	7.2	5.0	100	16.2	81.7	0.5	0.6	68.7	100
40	21.2	65.3	8.0	5.5	6.3	100	16.7	80.3	1.6	1.4	32.5	100
50	19.3	68.0	7.1	5.6	6.8	100	13.9	82.6	1.7	1.8	27.2	100
60	19.6	62.8	9.4	8.2	4.7	100	12.1	81.1	3.4	3.2	14.2	100
70	19.6	60.4	11.2	8.8	4.0	100	12.3	82.4	2.7	2.6	17.9	100

Initial concentrations: $\text{DON}^{\circ} = 0.23$; $N_{\text{D}}^{\circ} = 0.01$; $\text{NH}_4^{\circ} = 0.01$; $\text{NO}_2^{\circ} = \text{NO}_3^{\circ} = 0$; $B_1 = 5.10^{-7}$; $B_2 = 3.10^{-8}$; $B_3^{\circ} = 10^{-4}$ (all mgN/l)

Table 17. Influence of plankton decomposition in darkness on compound composition of the media (results from modeling).

Time in days	Relative concentrations of nitrogen compounds (%)						
	N _{soluble}		Nitrogen soluble	N _{particulate}		Nitrogen particulate	Mass balance
	DON	N _{mineral}		N _{living}	N _{detritus}		
0	0	0	0	100.0	0	100.0	100
2	11.4	0	11.4	55.2	33.4	88.6	100
4	19.9	9.3	29.2	33.2	37.6	70.8	100
10	25.6	22.5	48.1	20.9	31.0	51.9	100
14	37.6	16.5	54.1	19.9	26.0	45.9	100
20	39.8	15.8	55.6	19.9	24.5	44.4	100
24	34.8	19.9	54.7	20.0	25.3	45.3	100
30	32.2	23.4	55.6	19.1	25.3	44.4	100
34	32.0	27.9	59.9	16.6	23.5	40.1	100
40	29.2	37.8	67.0	12.9	20.1	33.0	100
50	29.0	41.6	70.6	13.1	16.3	29.4	100
60	32.5	30.2	62.7	17.1	20.2	37.3	100
70	32.6	21.1	53.7	19.9	26.4	46.3	100

1948). In experiments with sea water (Brand, Rakestraw, 1941), already discussed in this report, the change of nitrogen concentration in particulate matter has been taken into account. This information allowed us to judge the upper bound of the sum of particulate nitrogen forms during the whole experimental period. Since there is no information on nitrogen concentrations in particulate matter in tests with lake water, it was decided to examine some of the consequences of plankton decomposition in darkness, as well as the influence of this process on nitrogen transformations.

Plankton decomposition develops more actively than the transformation of these chemical forms of nitrogen considered in this model. This conclusion was made on the basis of analyzing numerous literature sources including those with data on plankton decomposition and influence of this decomposition on the composition of the compound in the water (Golterman, 1964;

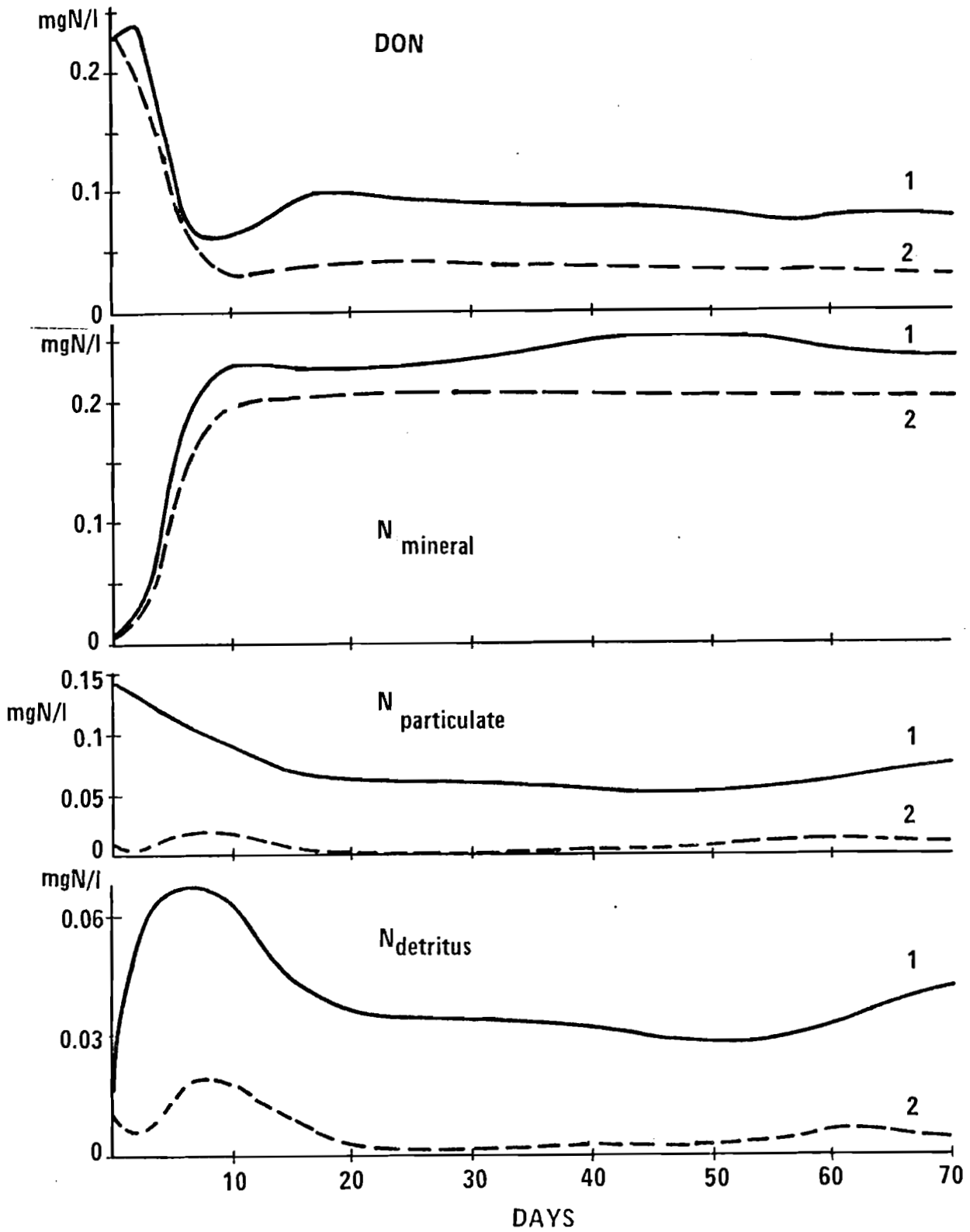


Figure 14. Dynamics of nitrogenous compound in water with decomposed plankton (curves 1) and without it (curves 2), Model 2.

Skopintsev et al, 1965). The analysis of the available data shows that plankton decomposition is accompanied by an increase of detritus and DON concentrations during the first few days of incubation. Because there are no quantitative data on these nitrogenous forms (Votintsev, 1948) various initial concentrations for detritus and DON were used to examine the influence on subsequent transformations of the nitrogen compounds.

In the first simulation run (version 1) the DON content was assumed to be high while in the second run (version 2) DON and detritus concentrations were assumed to be approximately equal. The results of the model, which simulate the dynamics of nitrogen transformations in lake water with different initial concentrations of DON and detritus, are compared with the experimental data of Votintsev (1948) in Figures 15 and 16. The input data used for these runs are presented in Table 18. It appears from the information in Figures 15 and 16 that both runs are in agreement with the experimentally observed picture of nitrogen compound transformations. Values of maximum growth rate, the elimination and liberation activity for heterotrophs were varied in the model (Table 18).

Thus, Model 2 can be used not only for a quantitative estimation of water quality, but also for testing existing theoretical hypotheses aimed at explaining the transformation of substances in the various water media.

7. GENERAL DISCUSSION OF SIMULATION RESULTS

It is interesting to analyze those values for parameters that were changed for the different simulations. Table 19 shows that in various tests the initial concentrations of the nitrogen compounds were different. It should be noted that values of biomasses and constants which describe the bacterial dynamics were chosen to meet the condition of comparing simulation results with the experimental data. All constants in Table 19 reproduce the bacterial function which corresponds to the experimental data on nitrogen compound transformations. Some values for the constants differ quite significantly in the various water media (Table 19).

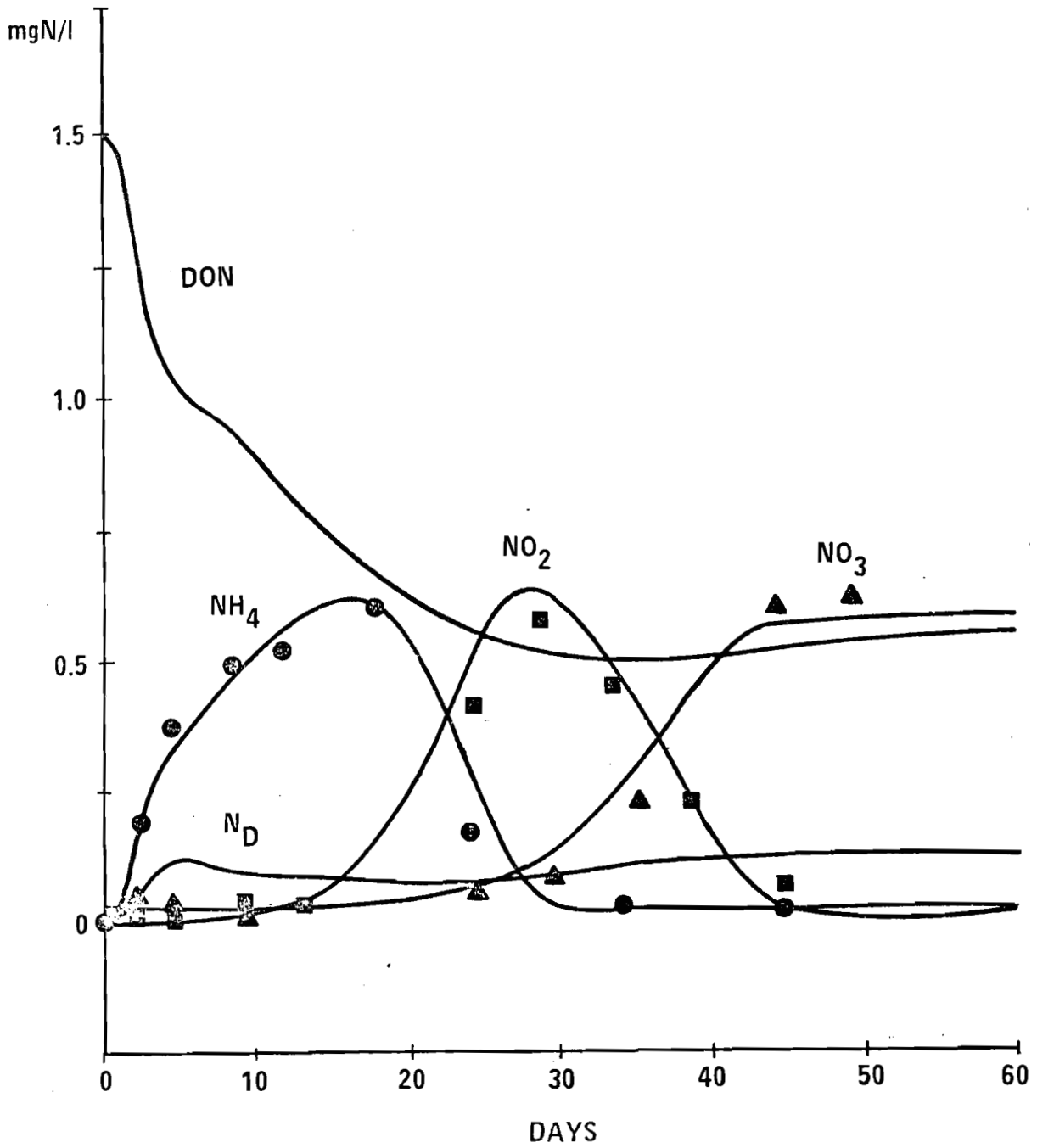


Figure 15. Comparison of simulation results (curves) with experimental data (points) of Votintsev (1948).
Model 2, lake water, input parameters in table 18, version 1.

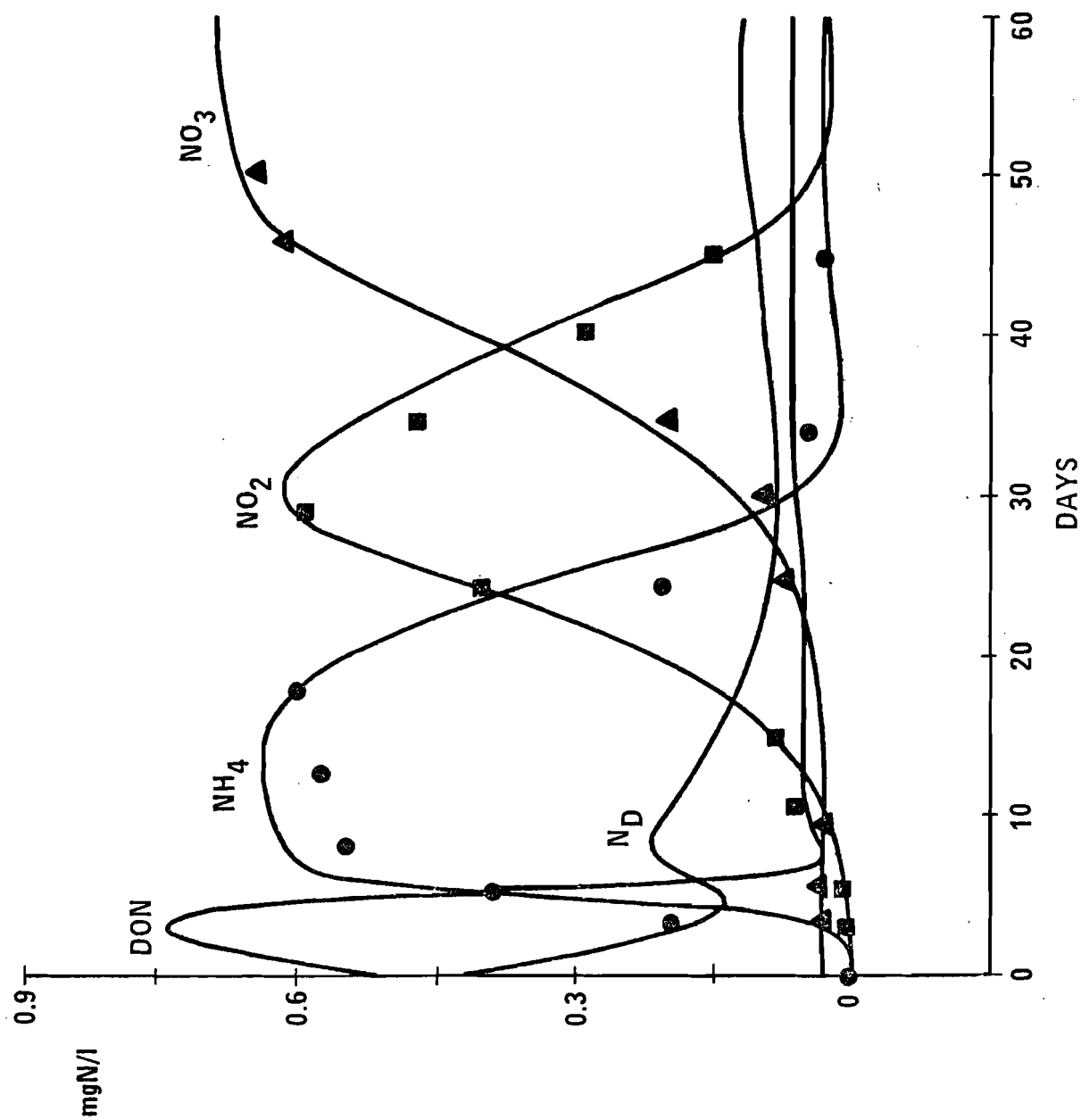


Figure 16. Comparison of simulation results (curves) with experimental data of Votintsev (1948). Model 2, lake water, input parameters in Table 18, version 2.

Table 18. Initial concentrations of nitrogen compounds for lake water and constants used in modeling (for Figures 15 and 16).

Nitrogen compounds	Values		Parameters	Values		Parameters	Values	
	1	2		1	2		1	2
DON	1.5	0.5	K_{1-2}	-	-	G_{12}	0.8	0.6
NH_4	0.001	0.001	K_3	7.5	22.0	G_{13}	0.4	0.5
NO_2	0.002	0.002	K_4	4.0	8.0	G_{14}	75	75
NO_3	0.03	0.03	K_5	14.4	20.0	G_{15}	1.05	1.05
N_D	0.01	0.45	K_6	0.015	0.015	G_{16}	1.0	1.0
B_1	7.10^{-4}	7.10^{-4}	K_7	-	-	G_{17}	1.25	1.25
B_2	8.10^{-3}	$8.5.10^{-3}$	K_8	0.4	0.4	G_{18}	700	0
B_3	8.10^{-5}	8.10^{-5}	K_9	0.0	0.0	q_{1-2}	-	-
PL1	0	0	d_{1-13}	-	-	q_3	1.0	1.0
PL2	0	0	a_{1-4}	-	-	q_4	1.0	1.0
M_{B3}	0	0	a_5	2.25	2.25	q_5	1.0	1.0
			a_6	2.32	2.32	q_6	-	-
			a_7	3.0	3.0	q_7	1.0	1.0
			a_8	3.093	3.093	q_8	1.0	1.0
			a_9	0.0073	0.28	q_9	0.97	0.97
			a_{10}	0.0182	0.31	q_{10}	0.03	0.03
			G_1	1.5	1.5	q_{11-14}	-	-
			G_2	2.0	2.5	q_{15}	1.0	1.0
			G_3	0.14	0.14	q_{16}	13.35	13.35
			G_{4-7}	-	-	q_{17}	1.0	1.0
G_8	0.12	0.22	q_{18}	3.42	3.42			
G_9	0.0	0.0	q_{19}	1.0	1.0			
G_{10}	0.08	0.15	q_{20}	1.14	1.14			
G_{11}	0.0	0.0	q_{21-26}	-	-			

Parameters for plankton not listed.

Table 19. Summary table of parameters which were varied in modeling nitrogen transformations in different waters.

Parameters	Sewage	River water	Sea water	Lake water	
				version 1	version 2
DON	2.7	0.5	0.23	1.5	0.5
NH ₄	10.8	17.5	0.01	0.001	0.001
NO ₂	0	0.25	0	0.002	0.002
NO ₃	0	0.1	0	0.03	0.03
N _D	0.1	0.01	0.01	0.01	0.45
B ₁	0.065	1.5·10 ⁻³	5.10 ⁻⁷	7.10 ⁻⁴	7.10 ⁻⁴
B ₂	0.5	8.10 ⁻³	3.10 ⁻⁸	8.10 ⁻³	8.5.10 ⁻³
B ₃	0.04	0.04	1.10 ⁻⁴	8.10 ⁻⁵	8.10 ⁻⁵
PL2	0	0	0.14	0	0
M _{B3}	0.02	0.02	0	0	0
K ₂	-	-	70	-	-
K ₃	11	25	330	7.5	22
K ₄	12	30	300	4	8
K ₅	105.6	105.6	74	14.4	20
K ₆	0.025	0.02	0.015	0.015	0.015
K ₈	0.4	0.4	0.05	0.4	0.4
d ₁₀	-	-	7.10 ⁻⁴	-	-
d ₁₁	-	-	3.10 ⁻⁴	-	-
d ₁₂	-	-	5.10 ⁻⁴	-	-
G ₁	0.5	0.01	15	1.5	1.5
G ₂	0.5	0.01	12	2	2.5
G ₃	5.0	5.0	0.5	0.14	0.14
G ₆	-	-	0.3	-	-
G ₈	0.1	0.2	0.1	0.12	0.22
G ₉	0.05	0	0.12	0	0
G ₁₀	0.3	0.15	0.05	0.08	0.15
G ₁₁	0.1	0	0.1	0	0
G ₁₂	0.8	0.2	0.5	0.8	0.6
G ₁₃	0.4	0.4	0	0.4	0.5
G ₁₄	75	75	85	75	75
G ₁₈	700	300	100	700	0

(contd.)

Table 19 (cont'd)

Parameters	Sewage	River water	Sea water	Lake water	
				version 1	version 2
a_3	-	-	0.2	-	-
a_4	-	-	0.202	-	-
a_5	1.5	0.5	1.7	2.25	2.25
a_6	1.875	0.67	1.828	2.32	2.32
a_7	2.1	1.0	1.7	3	3
a_8	2.62	1.39	1.828	3.093	3.093
a_9	0.0085	0.0073	0.06	0.0073	0.28
a_{10}	0.0121	0.0182	0.15	0.0182	0.31

If experimental data on the changes in concentration of only the chemical components are available, the transformation activity of the organisms can be reliably reproduced and reconstructed. For the mathematical modeling of water quality in ecological systems it is important to have quantitative information on the changes in transformation activity of these biological populations. From a practical point of view these characteristics are more important for water quality analysis than the biomass values of the organisms which take part in the transformation of chemical compounds of different origin. Detailed data on chemical compound transformations also allow examination of the sufficiency of those prerequisites that are used for constructing the model for organism activities. Additional information on microorganism concentration changes will assist in correcting the values for the constants for growth of the populations.

In the present experimental studies such data are not available and therefore there can be no guarantee of the reliability of the selected values for the initial microorganism

concentrations and rate constants. However, if simulation results correspond to an experimentally observed picture of the chemical compound dynamics when data on biomass changes are absent, then the model can be regarded as reproducing the activity of the populations and their influence on the other components.

It is interesting to compare the values of the rate constants describing the bacterial growth, as used in this report, with literature values. As mentioned above, the Michaelis-Menten and Monod kinetic expression is usually used for describing bacterial growth or the uptake of chemical compounds by growing microorganisms in water quality and ecological models. This expression is

$$v = \frac{\mu \cdot N}{K_M + N} \quad (82)$$

where v is the rate of the process considered (day^{-1}); μ is the maximum growth (or uptake) rate (day^{-1}); K_M is the Michaelis constant (mgN/ℓ); and N is the substrate concentration (mgN/ℓ). The present model was constructed on the principles of biogeocoenosis modeling (Poletaev, 1968) and from models of the bacterial transformation of chemical compounds along the chain: substrate \rightarrow bacterial biomass \rightarrow excreted metabolic products (Ajzatullin, Leonov, 1975a, b; Leonov, Ajzatullin, 1975a, b). According to the scheme used in this study the biomass changes at each moment of time are defined by the difference between the specific rates of substrate uptake, the excretion of metabolic products and mortality. Therefore, for comparison of the rate constants used in this report with the constants of the Michaelis-Menten expression traditionally used for modeling bacterial growth we must couple the equations which describe the uptake and excretion of compounds by bacteria. After rearranging the corresponding equations of Model 2, we can consider, for nitrifying bacteria, the following expressions for μ and K_M :

$$\mu = \frac{K_i \cdot (a_j/a_{j+1})}{G_k + a_{j+1} \cdot K_i} \quad (83)$$

$$K_M = \frac{1}{G_k + a_{j+1} \cdot K_i} \quad (84)$$

where $i=3$; $j=5$ and $k=1$ for Nitrosomonas; $i=4$; $j=7$ and $k=2$ for Nitrobacter. For heterotrophic bacteria, the values of μ and K_M at each moment of time will be the corrected values of M_{B3} ; the equations for recalculation of these constants as used in this study may be written as

$$\mu = \frac{K_5 \cdot (a_9/a_{10})}{G_3 + G_{18} \cdot G_3 \cdot M_{B3} + a_{10} \cdot K_5} \quad (85)$$

$$K_M = \frac{1 + G_{18} \cdot M_{B3}}{G_3 + G_{18} \cdot G_3 \cdot M_{B3} + a_{10} \cdot K_5} \quad (86)$$

Literature values (Sharma, Ahlert, 1977; Harleman, 1978) and rate constants recalculated from equations (83)-(86) as used in this report are presented in Table 20. All values of the kinetic constants used in this study correspond to the range of values reported elsewhere (Sharma, Ahlert, 1977; Harleman, 1978; Beck, 1978).

The process of substrate consumption by growing organisms and the growth of the organisms cannot be regarded as equivalent processes, because not all of the utilized substrate is included in the biomass. Metabolized substrate undergoes transformations. The majority of metabolized substrate is excreted in the form of waste products, while only a small portion is absorbed into the organisms' cells (biomass). In modeling population growth kinetics, using Michaelis-Menten or Monod expressions, this feature of the organisms is taken into account by means of introducing a special constant, i.e. the yield coefficient Y .

Table 20. Comparison of rate constants used for modeling bacterial dynamics (with literature data).

Authors of Experiments	Type of Water	M A T H E M A T I C A L M O D E L I N G					Reference
		Bacteria	Initial Bacteria Biomass mg N/l	K_M , mg N/l	μ , day ⁻¹	Yield Coefficient	
De Marco et. al (1967)	Sewage	Nitrosomonas	0.065	0.053	0.425	-	in given report
		Nitrobacter	0.5	0.035	0.305	-	
		Heterotrophs	0.04	0.197-0.78	0.922-2.964	-	
Knowles et. al. (1965)	River Water	Nitrosomonas	0.0015	0.066	1.11	-	in given report
		Nitrobacter	0.008	0.026	0.517	-	
		Heterotrophs	0.04	0.174-0.19	1.09-2.887	-	
		Nitrosomonas	0.01 -0.05	0.06	0.7-1.2	0.05	Harleman (1978)
		Nitrobacter	0.015-0.02	1.7	1.1-1.8	0.02	
Brand, Rastraw (1941)	Sea Water	Nitrosomonas	$5 \cdot 10^{-7}$	0.002	0.495	-	in given report
		Nitrobacter	$3 \cdot 10^{-8}$	0.002	0.497	-	
		Heterotrophs	$1 \cdot 10^{-4}$	0.091-0.145	2.474-2546	-	
Votintsev (1948)	Lake Water	Nitrosomonas	$7 \cdot 10^{-4}$	0.058	0.382	-	in given report version 1
		Nitrobacter	$8 \cdot 10^{-3}$	0.076	0.266	-	
		Heterotrophs	$8 \cdot 10^{-5}$	1.139-2.576	6.23-14.09	-	
		Nitrosomonas	$7 \cdot 10^{-4}$	0.021	0.405	-	in given report version 2
		Nitrobacter	$8.5 \cdot 10^{-3}$	0.04	0.282	-	
		Heterotrophs	$8 \cdot 10^{-5}$	0.166	2.846	-	
Nitrosomonas	$4 \cdot 10^{-4}$	0.6	1.2	0.05	Harleman (1978)		
Nitrobacter	$7 \cdot 10^{-3}$	1.7	1.8	0.02			
Heterotrophs	$1 \cdot 10^{-4}$	0.15	1.0	0.2			
-	-	Nitrosomonas	-	0.06 -5.6	0.46 -2.2	0.03-0.13	Sharma, Ahlert (1977)
		Nitrobacter	-	0.06 -8.7	0.28 -1.44	0.02-0.08	
		Heterotrophs	-	1.00 -181	7.2 -17	0.37-0.79	
-	-	Nitrosomonas	-	0.002-0.066	0.382-1.11	in Table 21	in given report
		Nitrobacter	-	0.002-0.076	0.266-0.517	" " "	
		Heterotrophs	-	0.091-2.576	0.922-14.09	" " "	

This parameter shows which portion from the total transformation of substrate is bound to biomass (Sherrard, Schoeder, 1973; Harleman, 1978). The range of Y values for different organisms is presented in Table 20. Y is a physiological characteristic of the organisms and it cannot be considered as a constant value because it depends on numerous environmental factors. Perhaps Y can be regarded as a constant only in a limited interval of time measured by hours provided the environmental conditions do not change. Usually such conditions are created and maintained in microbiological reactors (or chemostats). Therefore, Y is considered to be constant in modeling population growth in such experimental systems; however, during the growth of the organisms Y changes by 4.5 times from 0.45 to 0.1 (Sherrard, Schoeder, 1973). Ijerusalimsky (1963) proposed some amendments for a kinetic model of substrate utilization and organism growth by using Y . He assumed that the total specific rate of substrate utilization provides for the growth of organisms and maintains their normal functioning in spite of nutrient limitations.

In modeling ecological processes for water quality, it is very important to include in the model parameters for describing microorganism dynamics, which are sensitive to all changes in the environmental conditions. The model itself must be capable of reproducing the main organism activities, i.e. growth, excretion and mortality. The desire to create the simplest model for describing a population does not always meet the demands of ecological research, where the influence of these populations cannot be disregarded. In modeling water quality processes, it is not sufficient to confine oneself to studying only certain organism functions, for example, studying only the consumption of compounds (Harleman, 1978). In ecological models the use of coefficients for excretion allows us to simulate the process of transformation of chemical compounds in detail (Ajzatullin, Leonov, 1975a, b; Leonov, Ajzatullin, (1975a,b).

This report also confirms that with the help of coefficients for excretion activity^{*}, nitrogen transformations can be

* parameters r_{B1} , r_{B2} , r_{B3}

reproduced in various water media. The values of these coefficients for different phases of bacterial growth are given in Table 21. These coefficients were obtained in modeling nitrogen transformations in various water media with the use of the above mentioned experimental data (De Marco et al, 1976; Knowles et al, 1965; Brand, Rakestraw, 1941; Votintsev, 1948). The phases of bacterial growth (Schlegel, 1972) are represented by the curves reflecting biomass changes. Values of the yield coefficient Y and excretion activity of bacteria (r_{Bi}) can be expressed by the following simple term:

$$Y_i = 1 - r_{Bi} \quad (87)$$

where $i = 1, 2, 3$ for Nitrosomonas, Nitrobacter and heterotrophs respectively.

As can be seen from Table 21, the excretion activity of organisms changes to a great extent not only in different water media, but also within a certain phase of population development. With abundant nutrients, the liberation activity of the nitrifying organisms in the lag-phase can be very high; simultaneously small amounts of consumed substrate (about 0.5-4%) are spent on constructing organism cells while the remainder of the substrate is excreted into the medium in a transformed form. Such conditions of nitrifying bacteria growth were observed in river water. With a comparatively low content of nitrogen compounds in the medium, the fractions of substances liberated by nitrifying bacteria can decrease; however, values of excretion activity have a very large range of variation, i.e. from 0.05 to 0.95. In periods of intensive development of the nitrifying bacteria (or logarithmic growth phase) their excretion activity fluctuates within a smaller range than in the former growth phase, since the average amount of substrate needed for biomass growth is larger. Small fluctuations of excretion activity are typical for the steady-state and mortality phases (Table 21). Simulation results show that on the whole heterotroph excretion activity fluctuates within a small range. In some cases, their values

Table 21. Values for excretion activity of bacteria (modeling).

Water	Bacteria	Growth phases of bacteria populations										
		Lag		Logarithmic		Biomass peaks		Mortality		Steady state		
		period (days)	r _{Bi}	period (days)	r _{Bi}	period (days)	mg/l	period (days)	r _{Bi}	period (days)	r _{Bi}	biomass mg/l
Sewage	Heterotrophs	0-5	0.31-0.33	5-6	0.31-0.32	6-7	0.26	7-10	0.31-0.32	10-30	0.32	0.16
	Nitrosomonas	-	-	0-8	0.52-0.97	-	-	-	-	-	-	-
	Nitrobacter	-	-	-	-	-	-	0-30	0.59-0.92	-	-	-
River	Heterotrophs	0-2	0.61-0.62	2-5	0.62-0.63	5-6	0.05	6-8	0.61-0.62	8-12	0.61	0.04
	Nitrosomonas	0-3	0.995-0.997	4-5	0.76-0.89	6	0.60	7-12	0.36-0.38	-	-	-
	Nitrobacter	0-3	0.96-0.97	4-7	0.96-0.997	8	0.19	9-12	0.42-0.45	-	-	-
Sea	Heterotrophs	0-1	0.873	2-5	0.75-0.87	6	0.017	7-12	0.7-0.75	13-70	0.74	0.003
	Nitrosomonas	0-24	0.9-0.97	25-70	0.7-0.97	-	-	-	-	-	-	-
	Nitrobacter	0-48	0.07-0.97	49-59	0.85-0.97	60	0.0045	61-60	0.73-0.78	-	-	-
Lake (version 1)	Heterotrophs	-	-	0-4	0.62-0.64	4	0.048	5-9	0.62	10-60	0.62	0.01
	Nitrosomonas	0-15	0.56-0.84	16-30	0.27-0.84	30	0.14	31-45	0.27-0.31	46-60	0.32	0.12
	Nitrobacter	0-25	0.05-0.74	26-45	0.17-0.76	45	0.16	46-60	0.16-0.2	-	-	-
Lake (version 2)	Heterotrophs	0-2	0.8-0.81	2-8	0.25-0.81	3	0.122	10-30	0.29-0.33	31-60	0.33-0.34	0.03
	Nitrosomonas	0-15	0.23-0.94	16-31	0.54-0.94	22	0.035	33-42	0.42-0.5	43-60	0.52-0.57	0.02
	Nitrobacter	0-30	0.07-0.76	31-48	0.55-0.85	49	0.052	50-60	0.32-0.42	-	-	-

can be assumed to be constant for the whole period of population development. These values are close to 0.32 for sewage, 0.62 for river water, and 0.75 for sea water. However, conditions set for heterotroph developments can significantly influence their excretion activity. For instance, these indexes for lake water can be assumed as constant values (approximately 0.62, version 1) or variable values fluctuating from 0.25 to 0.81 (version 2). This choice depends on the content of organic nitrogen in the medium.

The values of biomass at maximum (biomass peaks) and steady-state levels differ approximately by 1.2 - 5 times in various waters. It should be noted that by introducing a parameter for the excretion activity of organisms, the model managed to avoid obtaining false high biomass values, which are usually obtained with simplified ecological models. Biomass values in all the water media studied are comparatively small. For example, in different waters heterotroph biomasses fluctuate during the intermediate stages of population growth from 0.05 to 0.26 mg/l. The same parameters for Nitrosomonas and Nitrobacter equal 0.03 - 0.6 mg/l and 0.05 - 0.16 mg/l, respectively. At steady-state levels heterotroph and Nitrosomonas biomasses are equal, less than 0.1 mg/l in natural water, and fluctuate from 0.16 to 0.6 mg/l in sewage. A steady-state level for Nitrobacter development is not reached in the cases studied.

As a rule, in simplified ecological models, biomasses of bacteria are not taken into account for calculating mass balance. Organisms are considered as formal parameters which are introduced into the model only for reproducing the dynamics of chemical compounds. Sometimes, it is possible to obtain more or less true pictures of these dynamics (Harleman, 1978). However, it is hardly possible to obtain results that are in agreement with the experimental data for the whole period studied. Therefore, simplified models can be used only in limited situations. Moreover, in each case, it becomes necessary to modify not only the input parameters but also the model structure. However, the application of Model 2 for studying water quality processes allows not only the reproduction in detail of changes in chemical

$(UP_{Bi} \cdot B_i)$

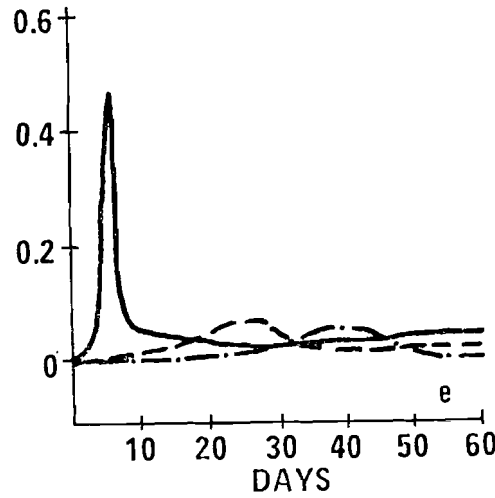
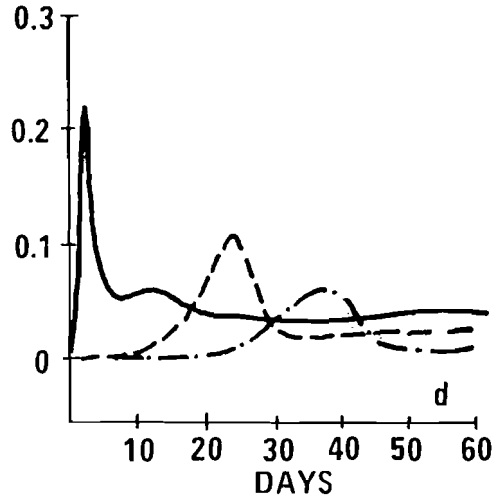
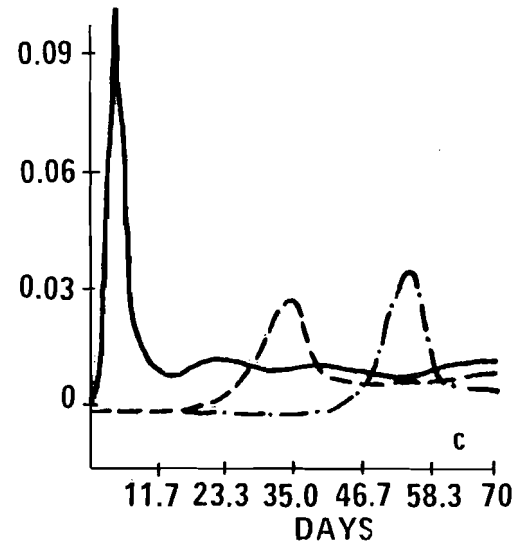
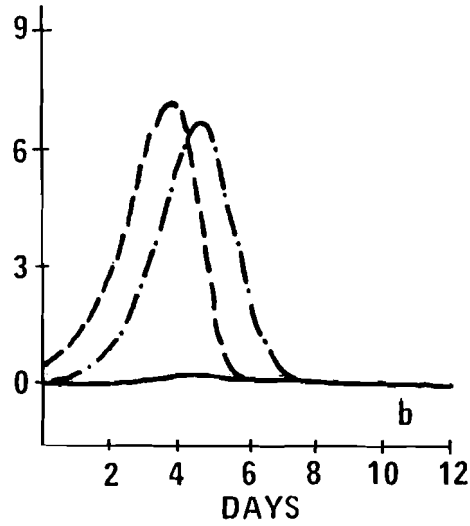
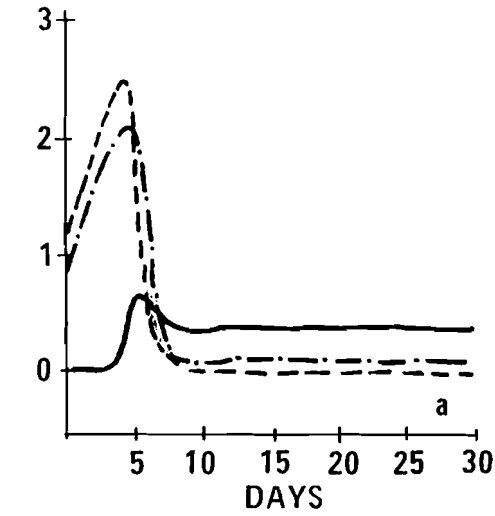


Figure 17. Change of oxidative activity for bacteria in various waters, Model 2:

- a. for sewage;
- b. for river water;
- c. for sea water;
- d. for lake water (version 1);
- e. for lake water (version 2);
- for Heterotrophs
- - - for Nitrosomonas
- · - for Nitrobacter

compound concentrations, but also an evaluation of the role of individual organisms in oxidation.

For example, Figure 17 illustrates the change of oxidation activity* of bacteria in different types of water. The greatest activity of heterotrophs was observed in sewage (curve 1, Figure 17a), while with nitrifying bacteria, this occurred in river water (curves 2 and 3, Figure 17b). The smallest values for oxidation activity of all bacteria were observed in sea water (Figure 17c), where concentrations of all nitrogen compounds are lower than in all other types of water. The alteration of initial conditions in modeling nitrogen compound transformations significantly affects oxidation activities by bacteria. Thus, in the case of lake water with different initial concentrations of dissolved organic nitrogen, values of the oxidation activity of heterotrophs and peak periods of these values vary (curve 1, Figure 17d, e).

Values of bacterial oxidation activity in the different water media may be considered quite reliable because the model very closely reproduced concentration changes in the nitrogen compounds as observed in experiments. However, one cannot say with confidence that values of biomasses and specific rates of substrate consumption are very accurately estimated by the model. To set accurate estimates of these values one should have experimental data on biomass population changes as well as data on nitrogen compound concentrations.

During recent years many attempts have been made to predict the influence of nitrogen transformations on the oxygen balance of natural waters. At present, there are different models which describe the kinetics of oxygen consumption conditioned by nitrification (Tuffey et al, 1974). The application of Model 2 and the use of experimental data on nitrogen transformation (De Marco et al, 1967; Knowles et al, 1965; Brand, Rakestraw, 1941; Votintsev, 1948) give an opportunity to estimate the dynamics of biochemical oxygen consumption (BOC) and the dynamics

* Product of multiplication of biomass on specific rate of nutrient uptake.

of dissolved oxygen concentration from the point of view of nitrogen transformation in different waters. Figure 18 shows BOC curves for ammonium oxidation (curve 1) and nitrite oxidation (curve 2) in different waters. The maximum amounts of oxygen spent in oxidizing ammonium and nitrite were observed in modeling for river water (Figure 18a) and the least for sea water (Figure 18b). In sea water, the presence of decomposing plankton (0.14 mg/l) increases by 1.5 times the amount of oxygen used for oxidation of ammonium and nitrite.

Simulation results show the dynamics of BOC for oxidizing dissolved organic nitrogen; they are presented in Figure 19 for different waters. For all the periods studied, the largest amount of oxygen used for organic nitrogen oxidation were observed in simulation runs for sewage (Figure 19a) and the least amounts for sea water (Figure 19b).

The dynamics of BOC for DON oxidation vary in different waters and they depend on the peculiarity of heterotroph growth. In sewage, some delay in BOC dynamics is observed during the first few days of water incubation. BOC dynamics in sewage and river water show that there is a considerably high storage of organic nitrogen in heterotrophic growth. After an initial adaptive period, the oxygen consumption develops at the rate of 1 - 1.5 mgO₂/l/day for 10-30 days in sewage and for 4-8 days in river water. In sea water, the oxygen consumption sharply slows down after the period of active heterotroph growth, which is finished by the 10th day. The oxygen consumption in sea water during 10-70 day periods proceeds at the rate of 0.106 mgO₂/l/day (with decomposing plankton) and 0.014 mgO₂/l/day (in the absence of plankton) (Figure 19b). The rate of oxygen consumption in lake water is higher because the concentration of DON in this system is also higher. In lake water, during a 15-60 day period, the oxygen consumption proceeds at a rate of about 0.35 mgO₂/l/day (version 1) and 0.25 mgO₂/l/day (version 2) (Figure 19c).

It should be noted that Model 2 reflects, as is already known from published literature, the peculiarities of BOC

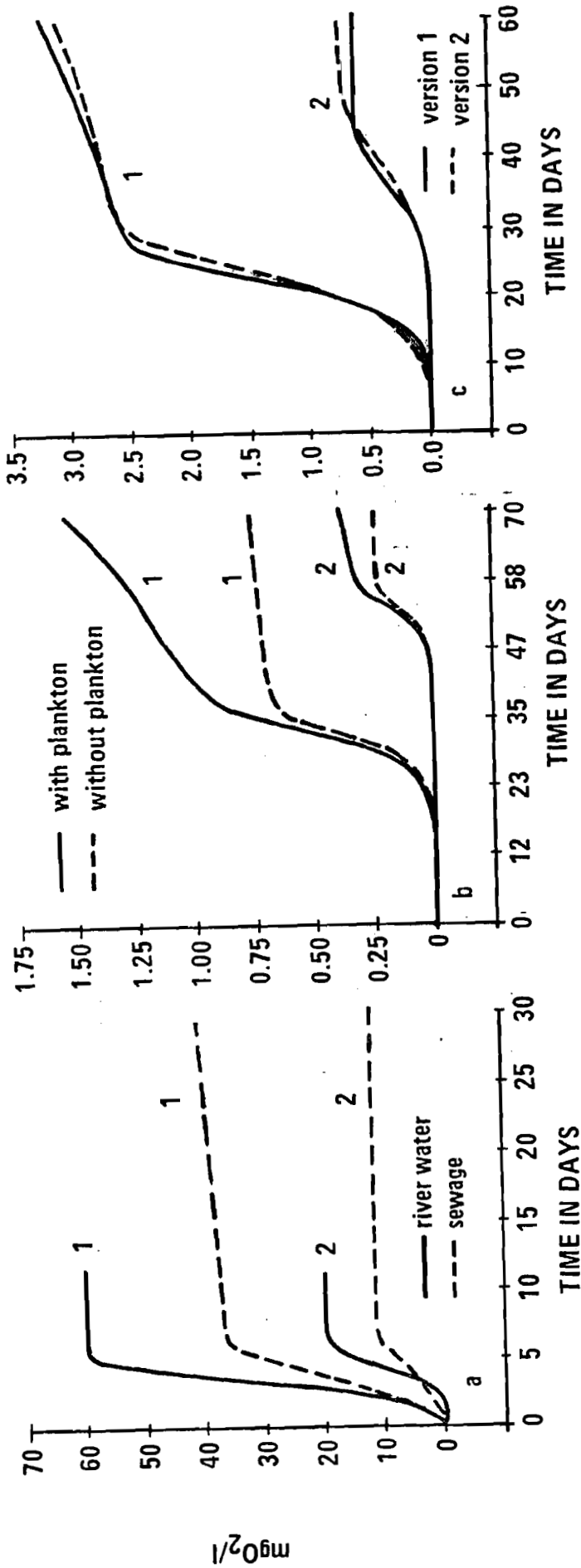


Figure 18. Dynamics of biochemical oxygen consumption for oxidation of ammonium (curves 1) and nitrite (curves 2), Model 2:
a. for sewage and river water;
b. for sea water with and without decomposed plankton;
c. for lake water.

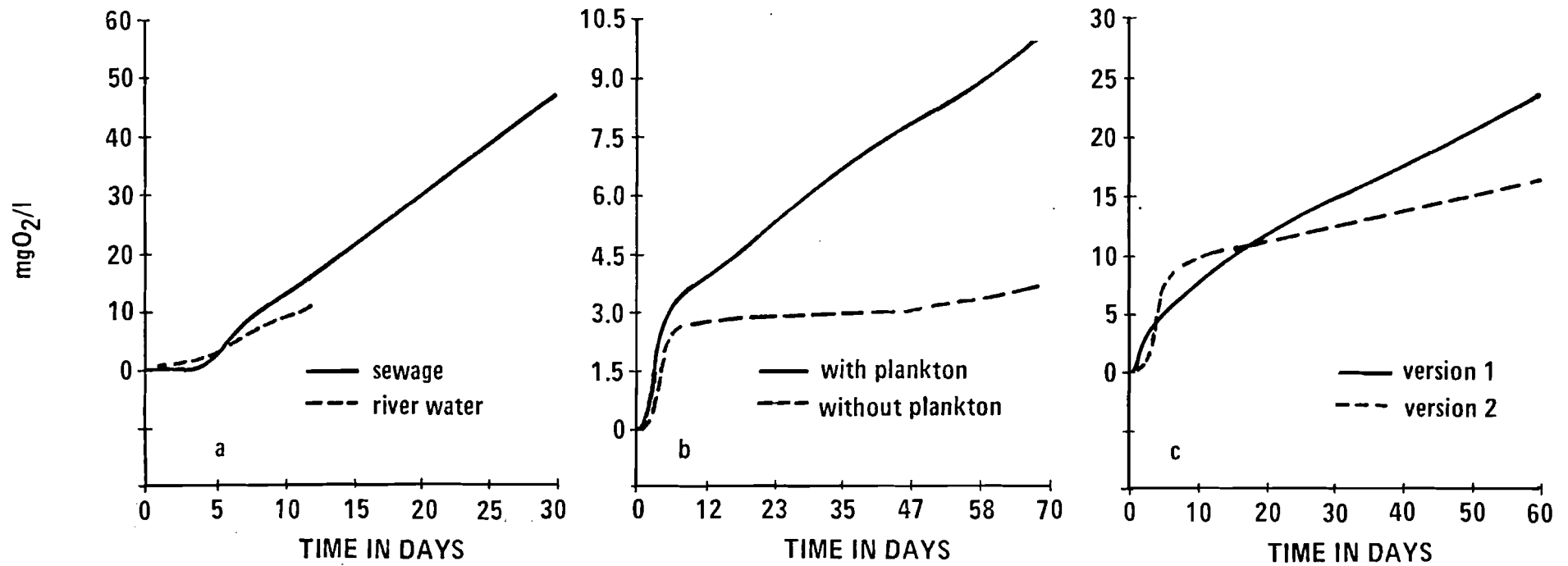


Figure 19. Dynamics of biochemical oxygen consumption for oxidation of dissolved organic nitrogen in various waters.

Model 2:

a. for sewage and river water;

b. for sea water with and without decomposed plankton;

c. for lake water.

dynamics, whose intensity depends upon organism respiration and substrate types* (Farcas, 1973). Simulation results show that in analyzing BOC data kinetics, formal subdivision of BOC into separate stages is quite justified (Leonov, 1974). The oxygen consumption by organisms sharply slows down with nutrient limitation. Model 2 represents the so-called stage of endogenous BOC (Brouzes, 1972; Gaudy, 1976).

Modeling also shows that data on BOC kinetics can give more useful information on transformation dynamics of dissolved organic matter (DOM) than even experimental measurements of DOM concentrations. For example, on the basis of curves representing DON concentration changes (Figures 10, 13, 15, and 16) it is hardly possible to draw conclusions about the ability of this compound to withstand bacterial decomposition after expiration of the first few days. DON concentration falls slowly in sewage (Figure 10). A low rate of DON concentration decrease is established in sea water after a 20 day period (Figure 13), in lake water after a 30 day period (version 1) or after a 10 day period (version 2) (Figure 15). As a matter of fact, heterotrophic bacteria continue to metabolize the labile matter and utilize oxygen. Using only experimental measurements of DOM concentration, it is very difficult to reveal this, since the bacterial utilization of DOM is balanced by its intake, at the expense of organism metabolic liberations and the decomposition of particulate matter.

Dissolved oxygen content, which depends in natural water on re-aeration and biochemical oxygen consumption, is used as a criteria of water quality and for evaluating the ability of organic matter to decompose. In estimating water quality in natural conditions by means of models, the task is to estimate the upper and lower bounds of variations in oxygen concentration and to assess BOC values within a given range of pollutant concentrations; the Streeter-Phelps model and its modifications, have been used for describing oxygen content decrease and for simulation of the oxygen sag (Ajzatullin, Lebedev, 1977). In

* Substrate are subdivided into labile, stabile and toxical.

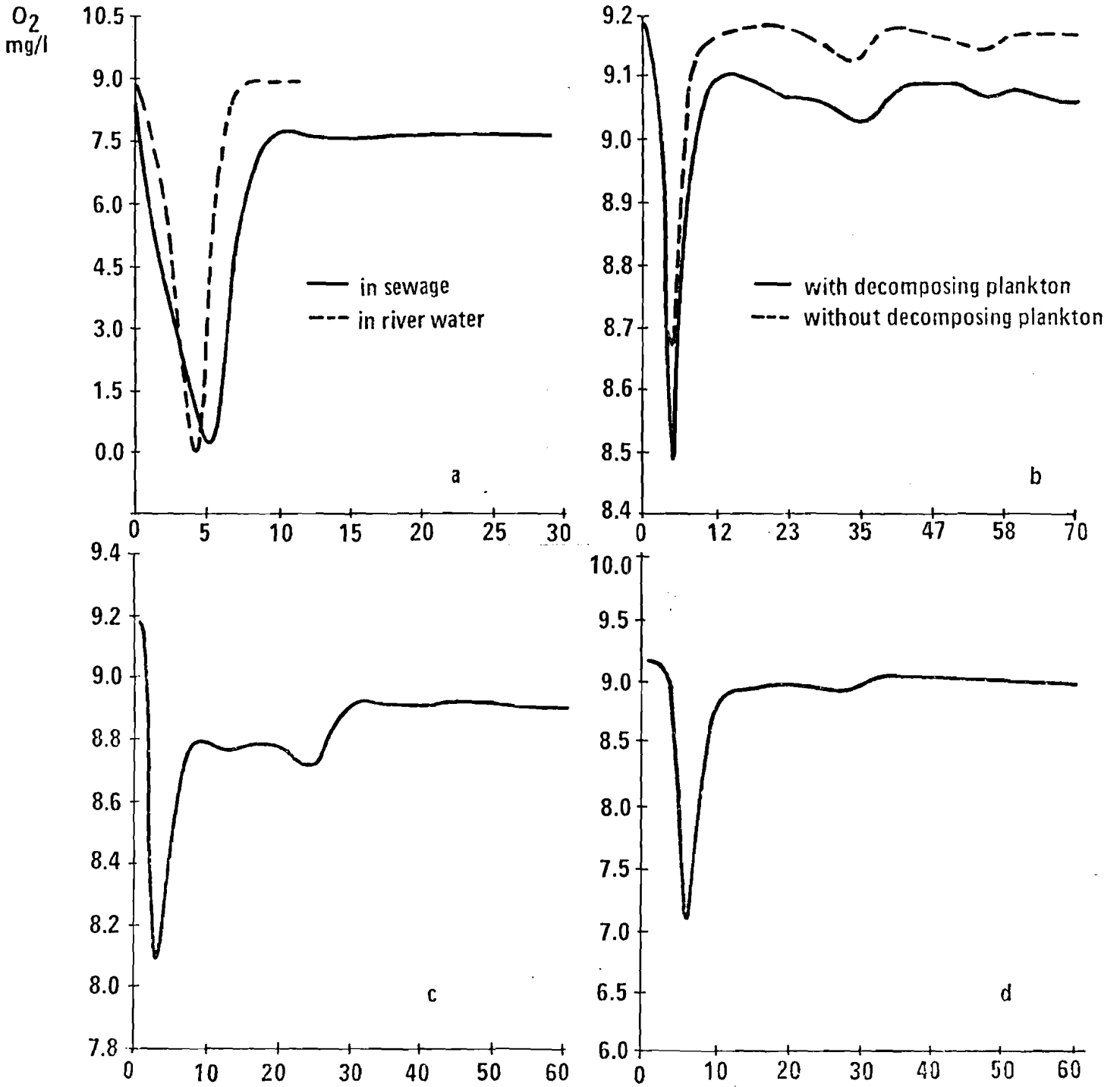


Figure 20. Dynamics of dissolved oxygen in various waters.
Model 2:
a. in sewage and river water
b. in sea water
c. in lake water (version 1)
d. in lake water (version 2)

this report, the curve of oxygen content was reproduced using experimental data obtained by different authors in studying nitrogen transformations.

Figure 20 shows simulation results which reflect the changes of dissolved oxygen concentration in various waters. The decrease of oxygen content in sewage and river water was caused by significant consumption during the oxidation of ammonium and nitrite (Figure 20a), while in sea and lake water this decrease is caused by oxidation of organic nitrogen (Figures 20b, c, d). Dissolved oxygen content decreases to $0.1 \text{ mgO}_2/\ell$ within 6-7 days in sewage and within 4-5 days in river water. In sea water the oxygen content falls from the saturation level ($9.2 \text{ mgO}_2/\ell$) to $8.5 \text{ mgO}_2/\ell$ (with decomposed plankton) and to $8.66 \text{ mgO}_2/\ell$ (without plankton) (Figure 20b). In lake water, the oxygen content decreases to $8.1 \text{ mgO}_2/\ell$ (version 1) and to $7.1 \text{ mgO}_2/\ell$ (version 2) (Figures 20c, d).

These modeling results show that, on the whole, in sewage, sea and lake water, aerobic conditions are maintained with the rate constant of re-aeration being $G_{17} = 1.25 \text{ day}^{-1}$. This value of rate constant was taken from the report of Sornberger and Keshavan (1973). For maintaining aerobic conditions in experiments with river water, the rate of re-aeration must be increased. Such conditions would be preserved if the re-aeration coefficient $G_{17} = 3 \text{ day}^{-1}$. The oxygen content is restored by re-aeration. After the restoration process is completed, the oxygen content in river, sea and lake water will be close to the level of saturation. In sewage, the oxygen concentration is less than the saturation level by an amount $1.7 \text{ mg}/\ell$ (Figure 20a). This fact shows how intense processes of oxidation are in sewage during the whole period studied. In sea water with decomposed plankton, the oxygen content after restoration is $0.2 \text{ mg}/\ell$ less than in the same water without plankton. In lake water, the restored oxygen content equals $8.9 - 9 \text{ mg}/\ell$ depending upon which version of the model is used (Figures 20c, d).

8. SUMMARY AND CONCLUSIONS

The mathematical models of nitrogen transformation presented in this report can be used for solving different problems in water quality assessment and for analyzing the state of water bodies. These models can be applied in connection with various objectives of research and for solving given, specific problems. The possibilities for model applications in describing water quality problems has been demonstrated in this report by comparisons with experimental data. Complex ecological models of biogeochemical cycles of nitrogen, which account for biological processes, can be used in practice for many types of problems encountered by scientists in connection with the study of water resources and their rational use. The models for nitrogen transformation presented in this report may be used for complex studies of questions of water quality, especially for such problems as (1) chemical and biochemical transformation of organic and mineral nitrogen compounds; (2) formation of particulate organic nitrogen and its transformation to dissolved organic nitrogen; (3) utilization of nitrogenous matter by plankton, including accounting for their preference for different nitrogenous compounds; (4) trophic interrelationships between plankton groups; (5) biochemical oxygen consumption for oxidizing organic and mineral nitrogen compounds and for organism respiration; (6) photosynthetic production of oxygen and organic matter by phytoplankton; (7) assimilation of particulate organic matter by zooplankton; (8) influence of temperature and light on plankton behavior; (9) influence of temperature on the rate of chemical and biochemical transformation of nitrogenous compounds.

The models considered in this report contain numerous different coefficients. Therefore it is difficult to estimate them. Without understanding the function of these coefficients and the mechanisms of transformation of nitrogen compounds, one can not use these models in practical studies. Special simplifications of these complex models may be easily made. Thus, the researcher can study separate transformation flows of the overall nitrogen cycle without disturbing the transformation mechanisms of individual nitrogen compounds. Simple models do

not have such possibilities because of the limited information used in them. They only reproduce the main properties and characteristics of real systems which tend to be only those features of importance for decision-making with the limited objectives applied to water quality problems. At the same time, everyone strives to receive as complete information as possible on the state of water quality, using relatively few parameters. Thus, the application of simple models does not in practice give any advantages in studying and understanding ecological processes in natural conditions because in each individual case, simple models have to be modified in order to fit the specific conditions of any given study.

The methods of systems analysis, as used here, and a knowledge of the mechanisms of chemical matter transformations, allow the construction of detailed models for solving water quality problems in aquatic systems. The realization of these models on computers offers the possibility of simulating natural aquatic system behavior in a broad spectrum of media state; thus, it is possible to solve different questions of water quality assessment by using chemical, biological and physical features of the system.

In this respect, it is shown that models, constructed on the basis of the transformation mechanism of chemical compounds, have a much greater simulation capability. However, at the present time, these models cannot be considered completely adequate for the ecological processes which they describe, although they simulate nitrogen compound transformation in some detail. The application of these models can be regarded as a successful exercise in modeling complex oxidation processes. The absence of multi-faceted experimental observations specially performed for determining the bounds of model adequacy, impedes the development of applied research in water quality modeling. There is, in particular, little knowledge of the concentration of biological compounds. To a great extent this fact impedes the quantitative estimation of the model parameters that describe the physiological features of these biological populations. At

present, the values of these characteristics are selected so that simulation results match experimental data on concentration changes of chemical compounds.

The complex ecological models presented here, can also be applied for constructing models of combined biogeochemical cycles of carbon, phosphorous and oxygen and for simulating aquatic ecosystem behavior and the processes of self-purification.

9. PROSPECTS FOR FUTURE RESEARCH AT IIASA

In recent years large-scale models have been developed for simulating processes under conditions that are very near to reality (Bernier, Ruszniewski, 1971; Bloomfield et al, 1973; Sanders, Falko, 1973). Such models are used for predicting the dynamics of purification and the effects of pollutants on ecological systems. During the first stages of development such models may be considered as a link between studies of micro-scale processes under laboratory conditions and macroscale processes under natural conditions (Ajzatullin, Lebedev, 1977). These models have been developed specifically for evaluation of the adequacy of laboratory experiments in studies of natural phenomena. However, as it has been noted in a very detailed review of mathematical models by Ajzatullin, Lebedev (1977), sufficient criteria for model adequacy have not yet been established. Three criteria of model adequacy can however be recognized as most representative (Pollak, 1969):

1. coincidence of experimental data to simulation results;
2. accordance of simulation results with indirect estimations which are not taken into account in model identification;
3. independence of rate constant values of individual stages from input concentration values.

For model verification the use of all three criteria is obligatory. It is absolutely essential for understanding the adequacy of a model and for determining the real bounds of its application (Ajzatullin, Lebedev, 1977). At present the criteria of adequacy are not used, or only one of the criteria is applied, for instance, in checking the agreement between

simulation results and a set of experimental data. Satisfaction of this set of criteria is the most vital problem of all current research on water quality modeling. This is also necessary for distinguishing the perspectives of mathematical models for water protection and for the rational use of water resources. If this problem can be solved, it would be possible to develop flexible mathematical models that would find application in predicting the processes of purification dynamics and the management of water quality (Ajzatullin, Lebedev, 1977).

For prospective studies at IIASA, one can suggest that construction of models for biogeochemical cycles of phosphorus and carbon and the verification of these models is important. It would be reasonable to conduct special research on modeling the combined transformation of biogenic compounds in water quality problems, especially for individual lakes and reservoirs. These studies should include a comparison of various simulation results obtained from different models for the same observations.

The methodological approaches in solving water quality problems by means of mathematical modeling are diverse. IIASA's task here is to choose the most rational way to solve this problem. This is connected to the complexity of the problem which must be considered to construct a given water quality model. A valuable water quality model should consider the following phenomena: purification processes, eutrophication, productivity and destruction processes, growth of micro-organisms responsible for the transformation of chemical compounds, biochemical oxygen consumption and dissolved oxygen regime, etc.

At present it is necessary to evaluate models against experimental laboratory data received in the batch (or chemostat) systems. Then these models should be expanded for studying the ecological processes under natural conditions, with parameters describing turbulent exchange, mixing, diffusion, convective transport, and other features of the water bodies. An example of these modeling efforts is the report by Beck (1978).

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