THE STUDY OF NITROGEN TRANSFORMATION IN FRESH WATER: EXPERIMENTS AND MATHEMATICAL MODELING

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PREFACE

The IIASA Working Paper entitled The Chemical-Ecological Modeling of Acquatic Nitrogen Compound Transformation Processes (WP-80-86) described mathematical models of nitrogen transformations which may be used for studying aerobic nitrogen cycling in different water environments. The possibilities of applying nitrogen models in experiments with sewage, river, lake and sea water samples were examined. This paper gives experimental data on nitrogen transformations in water withdrawn from Slnava Reservoir in Czechoslovakia. It also briefly reports on the nitrogen model which describes the bacterial conversion of nitrogen forms and is an example of the application of this model in the analysis of nitrogen transformation observed in experiments. The analysis of experimental data is considered essential to the identification of rate coefficients and it is assumed that it is quite important to perform this step of model examination before the model is applied in a simulation study of nitrogen transformation in a water body, under natural conditions.

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ABSTRACT

Two main transformations occur in water environments--one due to the effect of microorganisms and the other due to chemical reactions. Both transformations are very closely interwoven. Of the transformation processes in the water environment, nitrogen transformation is perhaps the most interesting because nitrogen and its compounds (both organic and mineral), affect the development of practically all aquatic microorgamisms and therefore determine the trophic state and the quality of a water environment. Nitrogen compounds are present in sewage and other waste water discharged into water bodies. Therefore, it is quite understandable why during the last few years nitrogen transformation is the subject of study at descriptive and experimental levels, as well as by mathematical modeling techniques. This paper reports on the results of a collaborative study between IIASA and the Institute of Experimental Biology and Ecology of the Slovak Academy of Sciences in Bratislava, on nitrogen transformations. The data of twelve experiments covering

a broad set of initial conditions in nitrogen concentrations and at two temperatures (18° C and 12° C) are presented in this report. These experimental data were analyzed with the help of the mathematical model developed at IIASA (WP-80-86) and intended for understanding processes of nitrogen transformation in water environments. The results of model description of nitrogen compound dynamics are evaluated by statistics to find a quantitative criteria in model assessment. In the discussion of simulation results, attention was focused on the analysis of bacterial activities in the conversion of organic as well as mineral nitrogen forms. The results reported here are considered to be the basis for the simulation of nitrogen dynamics in water bodies and for studying various aspects of ecology and aquatic ecosystem behavior.

CONTENTS

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INTRODUCTION

The problem of water quality is one of the most important for water resources management within Czechoslovakia because of the potential water shortage in this country. The river Danube and its tributaries, such as the Váh, Morava, Hron and Ipel´, are the basic water supply sources in Czechoslovakia. From the water management point of view, the most important river of the Slovakian part of the country is the River Váh. Its length is about 435 km, the difference in altitude between its source and the point it enters the Danube is 556 m. The watershed area of the River Váh is 11601 km^2. One of the largest water reservoirs, named Slanava reservoir, with an area of 4.3 km^2, was constructed on the River Váh, in order to meet the growing water demands within Slovakia. At present, the water from the river Váh is used for electricity production, for industry as well as for agriculture. With respect to water quality, only a limited section of the river at the upper part of the Váh watershed--up to Liptovský Mikuláš--is suitable for supporting fish. More

than 90 sources of pollution of the river Váh watershed area have been identified. The chemical, leather and wood industries are the main sources of organic pollution. The cellulose plants in Ružomberok, Martin and Žilina, the chemical complex in Šala and the leather plant in Liptovský Mikuláš are the key sources of pollution. A great number of pollutants come from the food industry, especially from the plants in Leopoldov, Trenčín, Sládkovičovo, Trnava, Boleráz and Chynorany. The coal mines in Handlová and Nováky, and the foundaries in Široká, Istebné and Sereď discharge insoluble material. Extensive settlement around the river also contributes to the pollution, by way of municipal or communal waters. A considerable share of the pollution results from diverse agricultural activities, which include the storage of chemical substances, and the service and maintenance activity connected with agriculture.

Among the pollutants of water bodies within Czechoslovakia, the role of nitrogen compounds, organic as well as mineral, is recognized as being quite important. It is estimated that the input of nitrogen compounds from the watershed area to the river Váh exceeds the phosphorus input by more than 10 times (Annual Report, 1980). In many cases, the presence of nitrogen compounds, from different sources determine the levels and state of water quality, because the concentrations of the main nitrogen compounds influence the development of practically all forms of life in the water environment and have a significant effect on the oxygen balance within the water body.

In the past decade, the fate of nitrogenous compounds in the water, as well as its role in the behavior of the water-ecological systems, has been studied by many scientists

(Brezonik, 1972, 1973; Keeney, 1972; Harrison, 1974). Currently, the available knowledge on nitrogen transformation in water environments and water bodies is used for the study of important problems, such as pollution of the water body, its self-purification, primary production and eutrophication, its ecological state and the significance of water microorganisms in the turnover, mineralization and conversion of the compounds of different origin. In the past few years, mathematical modeling has been widely used for the study of these limnological problems.

Examples of applying models to solve water quality problems on the basis of nitrogen transformations studies, have been given by Thomann et al., (1971), Anderson et al., (1976), Najarian and Harleman (1977), Shima et al., (1978), Knowles and Wakeford (1978), Casapieri et al., (1978), and Beck (1979). The extent of detail in the nitrogen transformation processes modeled, is defined by the objectives of the study, as well as by different research approaches.

It must be noted that many of the important questions related to the specificity of nitrogen transformation in the water bodies are still insufficiently studied. As a rule, the purposes of studying and modeling the compound transformations, and particularly nitrogen transformation in water bodies, requires interdisciplinary efforts and a wide variety of experimental studies. Problems such as nutrient availability for the different types of microorganisms, the contents of growth-limiting nutrients, and the specificity of nitrogen cycling due to a variety of microorganism species in the different environmental conditions remain to be elucidated (Keeney, 1972).

Nitrogen transformation in water has long interested biologists and chemists; it might be assessed in different ways but it seems reasonable to claim that it is defined by complex interrelationships between chemical and biological compounds and regulated by physical factors. Among all the processes involving the transformations of nitrogen compounds, the microbiological decomposition of nitrogenous matter takes priority when studying questions of water quality and particularly the self-purification ability of water environments. This particular process, and the complete nitrogen cycle, have been studied in experimental systems (Brand et al., 1937; Brand and Rakestraw, 1941; Votintsev, 1948; Golterman, 1960; Knowles et al., 1965; De Marco et al., 1967). To have the possibility of an effective control of water quality, based on the nitrogen oxidative transformations, it is necessary to know to which degree the studied water body is degraded and to consider factors affecting changes of concentrations of the individual nitrogen. One of the most important tasks, is therefore the study of those microorganisms involved in the process of transforming substances (matter) and energy within a water environment. To solve these problems it is necessary to utilize an approach combining experimental studies and mathematical modeling. Thus the description and analysis of the nitrogen transformations observed in experiments by means of a mathematical model is considered an important step in improving the understanding of complex oxidation processes occuring under a broad set of environmental conditions.

The objective of the study described in this report is to estimate experimentally the intensity of microbiological transformations of nitrogen compounds in water samples from Reservoir Slanava, an important water source in Slovakia, and to analyze the experimental data by a mathematical model describing the nitrogen oxidation process.

Analytical Procedure

The water samples used in all of our experiments were taken from Slnava Reservoir on the river Váh near the town of Pieštany (Figure 1). The reservoir is situated at river km 94.3. The length of the reservoir is approximately 6 km and the maximum width 1.8 km. The volume of the reservoir is $12.3.10^6$ m^3 and the watershed area above the reservoir is $10.1.10^3$ km^2. The sampling program took place in October (1979), and February and April (1980). The water was taken from depths of 0-3 m of the reservoir near the shore, as indicated in Figure 1; sampling was carried out with a Friedinger sampler and the samples were subsequently transferred to a laboratory. Amounts of 20 litre aliquots of the water were distributed into aquaria equipped with aerators. All the aquaria were placed in dark conditions, three at 18^oC and three at 12^oC. To two aquaria at each temperature, ammonium, nitrite and nitrate were added in the same proportions as determined in the original water sample. The third aquarium at each temperature was maintained without addition of nitrogen compounds and served as the control. At about weekly intervals, aliquots of water were taken from the aquaria for chemical analysis as described below.

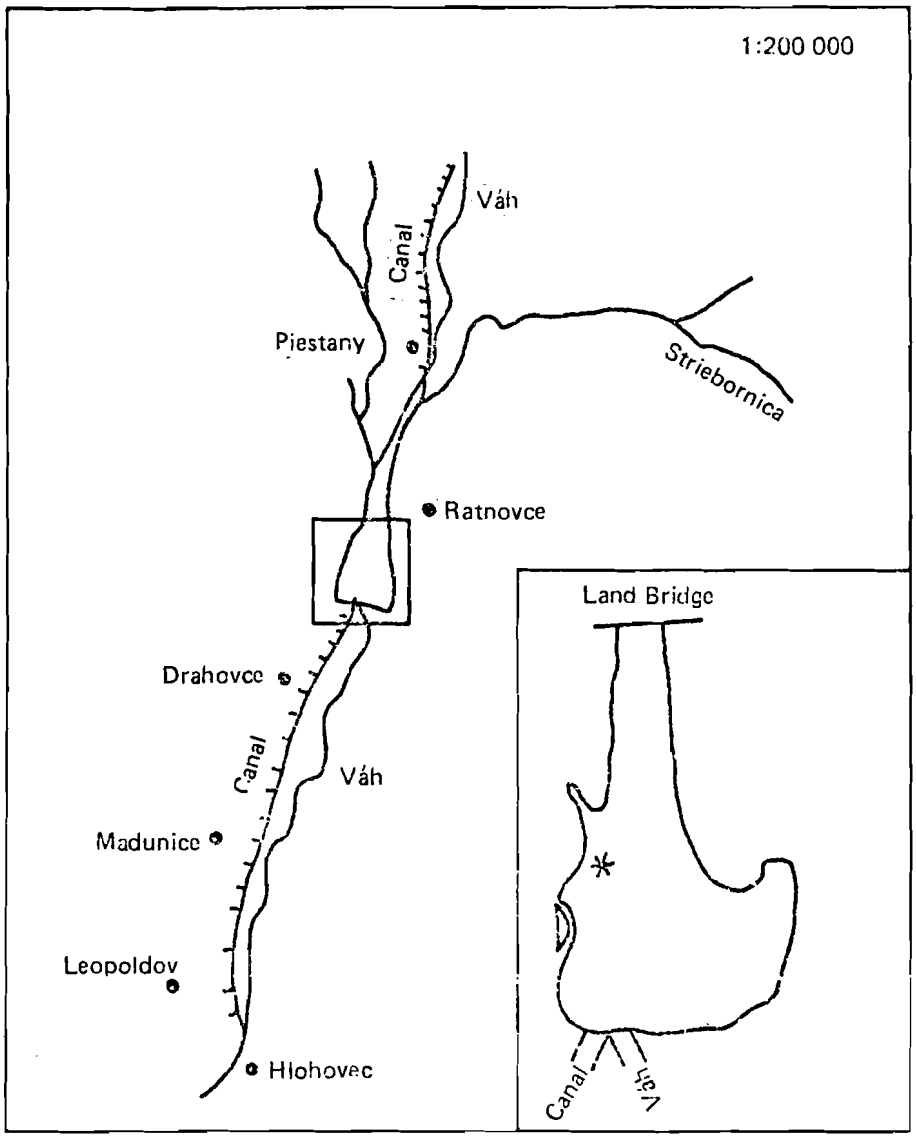

Figure 1. Map of the Slnava Reservoir vicinity; the sampling point is indicated by (*)

The water samples were handled as follows: (a) without treatment and (b) filtered through a Synpor membrane filter for determination of nitrogen compound concentrations by the methods mentioned as follows:

(1) Ammonium-nitrogen (NH_4^+-N):

For determination of ammonium concentration the colorimetric Nessler method was used. To avoid various types of interference the ammonium was predistilled from an alkaline water sample and then treated with K_2HgI_4 in alkaline solution producing a brownish-yellow complex compound.

(2) Nitrite-nitrogen (NO_2^--N):

The photometric method of Bendschneider and Robinson (1952) was used for nitrite determination. In a strongly acidic solution, nitrite reacts with sulphanilamide producing diazocompounds, which with N-(1-naphthyl)-ethylene-diamine-dihydrochloride gives an intensely colored azocompound.

(3) Nitrate-nitrogen (NO_3^--N):

Nitrate-N is reduced to nitrite in a strongly alkaline solution by hydrazine sulphate under the catalytic effect of Cu^{++}; the nitrite is then determined by method of Bendschneider and Robinson (1952).

(4) Dissolved Organic Nitrogen (DON):

The concentration of the dissolved organic-N was determined as the difference between the concentration of nitrogen forms measured by the Kjeldahl method and the concentration of ammonium-N in the water samples when filtered through a Synpor membrane filter with pore diameter 0.4 μm.

(5) Total Organic Nitrogen (TON):

The concentration of total organic-N was determined as the difference between the concentrations of nitrogen measured by the Kjeldahl method and of ammonium-N in the non-filtered water samples.

(6) Particulate Organic Nitrogen (PON):

The concentration of particulate organic-N was calculated as the difference of the total organic-N and dissolved organic-N.

(7) Total Nitrogen:

The concentration of total N was computed as the sum of all the forms of nitrogen compounds.

Taking into account the possible errors in procedure of sampling water from aquaria due to unequal distribution of various nitrogen forms in water medium and the errors connected with above mentioned analytical methods in nitrogen measurements combined with arithmetic calculations, it is assumed that the maximal deviations from the results received may be expected in the range of $\pm$ 15%.

Experimental Results

The experimental data on the nitrogen transformations at 18° C and 12° C in the water withdrawn from Slana Reservoir on 24.XI.79, 11.II.80, and 26.IV.80 are shown in Tables 1-4. The water samples in experiments 1,4,7 and 10 at 18° and 12° C without the addition of nitrogen compounds served as controls for the following analysis. All data in Tables 1-4 show that there is a marked difference both in the concentrations of all the nitrogen fractions in the water samples taken from Slnava Reservoir in the different months and development of nitrification under the various experimental conditions. The results in Tables

1-4 allow one to assume that the ammonium oxidation rates at 18° C, without any addition of inorganic forms of nitrogen (experiments 1, 7, and 10), are dependent on the time of sampling during the year. These rates are slowest in the February sample (experiment 7), when more than 50% of the initial amount of NH_4^+-N still remains in the water after 17 days of incubation. On the other hand in the October sample (experiment 1) only 14% of ammonium-N was found after 8 days of incubation.

It is generally supposed that there is a marked correlation between the ammonium-N decrease and the increase of nitrite-N levels in all experiments. However, on the basis of raw experimental results it is difficult to say that there are equivalent changes in the concentrations of ammonium-N and nitrite-N, but it is possible to recognize a time-dependence between decreasing ammonium-N concentrations and increasing nitrite-N levels.

Slight differences were found in the experiments as apparent in the February sample (experiment 7) when the nitrite-N peak was around the 9th day; in the April sample (experiment 10) this peak was found at the 7th day and in the October sample (experiment 1) at the 8th day. The concentration of nitrate-N approached a steady state level in the October sample by the 15th day of the experiment; in the April sample it was at the 35th day and in February water it obviously had to be later than at the 38th day, i.e. after the end of the experiment.

The addition of mineral forms of nitrogen to the water samples used in our experiments caused only slight changes in the rate of the nitrification process, as is shown in Table 1 for October, Table 3 for February and Table 4 for April.

Table 1. Changes of Nitrogen Compound Concentrations in mg N/ℓ at 18° C for Water Samples from the Slnava Reservoir. Sampling Date 24.X.79.

Experiment numbers	Nitrogen fractions	Period of Incubation							
		0	8	15	22	28	36	43	57
1	DON	0.71	1.73	1.05	1.03	0.78	0.87	1.12	1.05
	PON	0.90	0.42	0.13	0.30	0.48	0.35	0.35	0.29
	TON	1.61	2.15	1.18	1.33	1.26	1.22	1.47	1.34
	NH_4^+-N	1.80	0.254	0.015	0.05	0.01	0.006	0.031	0.022
	NO_2^--N	0.021	1.09	0.19	0.011	0.002	0.002	0.005	0.005
	NO_3^--N	0.049	0.512	2.24	2.06	2.05	2.07	2.10	2.32
	Total N	3.47	4.01	3.63	3.45	3.32	3.30	3.61	3.69
2	DON	0.71	0.78	1.18	1.03	0.81	0.60	0.60	0.57
	PON	0.90	1.00	1.41	0.88	1.15	1.24	0.81	1.06
	TON	1.61	1.78	2.59	1.91	1.96	1.84	1.41	1.63
	NH_4^+-N	4.35	3.44	0.25	0.19	0.15	0.09	0.051	0.075
	NO_2^--N	0.072	1.09	2.42	0.004	0.004	0.005	0.005	0.005
	NO_3^--N	0.40	1.18	2.32	3.19	3.83	3.62	3.86	3.93
	Total N	6.42	7.49	7.58	5.28	5.94	5.56	5.31	5.64
3	DON	0.71	0.76	2.89	3.77	3.13	3.85	3.80	3.57
	PON	0.90	1.94	8.41	6.48	8.30	5.69	3.66	2.08
	TON	1.61	2.70	11.3	10.25	11.4	9.54	7.46	5.65
	NH_4^+-N	30.3	30.6	0.39	0.15	0.04	0.054	0.041	0.15
	NO_2^--N	0.34	1.28	4.35	0.007	0.007	0.007	0.009	0.009
	NO_3^--N	1.15	2.14	15.1	20.3	20.2	21.1	21.8	22.2
	Total N	33.39	36.72	31.14	30.71	31.65	30.70	29.31	28.01

Table 2. Changes of Nitrogen Compound Concentrations in mg N/ℓ at 12° C for Water Samples from the Slnava Reservoir. Sampling dated 24.X.79.

Experiment numbers	Nitrogen fractions	Period of Incubation							
		0	6	13	20	27	34	41	55
4	DON	0.71	0.64	0.60	0.55	0.79	1.16	1.00	0.74
	PON	0.90	0.94	1.02	1.11	0.59	0.52	0.72	0.64
	TON	1.61	1.58	1.62	1.66	1.38	1.68	1.72	1.38
	NH_4^+-N	1.80	1.82	0.86	0.133	0.18	0.096	0.078	0.15
	NO_2^--N	0.027	0.063	1.09	0.004	0.009	0.024	0.02	0.018
	NO_3^--N	0.073	0.066	0.58	2.02	2.07	2.11	2.25	2.26
	Total N	3.50	3.53	4.15	3.82	3.64	3.91	4.07	3.81
5	DON	0.71	0.86	0.94	0.94	0.93	0.83	1.09	0.97
	PON	0.90	0.94	1.10	2.08	1.51	0.76	0.68	0.46
	TON	1.61	1.80	2.04	3.04	2.44	1.59	1.77	1.43
	NH_4^+-N	4.44	4.54	1.96	0.61	0.46	0.056	0.06	0.162
	NO_2^--N	0.086	0.15	1.59	0.013	0.013	0.027	0.004	0.027
	NO_3^--N	0.26	0.27	1.75	2.28	2.59	2.82	3.02	3.06
	Total N	6.39	6.76	7.34	6.14	5.09	4.49	4.85	4.68
6	DON	0.71	0.84	1.79	3.80	1.77	0.88	0.71	0.63
	PON	0.90	1.36	2.61	6.30	2.89	1.19	1.30	0.71
	TON	1.61	2.20	4.40	10.1	4.66	2.07	2.01	1.34
	NH_4^+-N	25.7	27.7	16.2	3.60	0.29	0.085	0.086	0.166
	NO_2^--N	0.37	0.33	2.64	0.225	0.022	0.025	0.002	0.033
	NO_3^--N	1.57	2.07	4.03	9.12	16.31	18.17	20.1	20.6
	Total N	29.24	32.30	27.27	23.05	21.28	20.35	22.20	22.14

Table 3. Changes of Nitrogen Compound Concentrations in mg N/ℓ at 18° C for Water Samples from the Slnava Reservoir. Sampling date 11.II.80.

Experiment numbers	Nitrogen fractions	Period of Incubation						
		0	2	9	17	23	30	38
7	DON	0.86	1.12	0.98	0.34	0.20	0.14	0.12
	PON	0.67	0.46	0.53	0.35	0.24	0.18	0.09
	TON	1.53	1.58	1.51	0.69	0.44	0.32	0.21
	NH_4^+-N	0.30	0.22	0.19	0.17	0.02	0.02	0.02
	NO_2^--N	0.014	0.019	0.17	0.025	0.003	0.002	0.005
	NO_3^--N	1.09	1.10	0.93	2.21	2.40	2.55	2.67
	Total N	2.93	2.92	2.80	3.10	2.84	2.89	2.89
8	DON	0.86	1.10	0.40	0.98	0.60	0.55	0.26
	PON	0.67	0.99	0.64	0.57	0.30	0.27	0.43
	TON	1.53	2.09	1.04	1.55	0.90	0.82	0.69
	NH_4^+-N	3.20	3.09	3.40	0.60	0.005	0.020	0.010
	NO_2^--N	0.147	0.13	0.32	0.02	0.02	0.01	0.01
	NO_3^--N	2.13	2.05	2.88	5.80	6.30	6.80	6.73
	Total N	7.01	7.36	7.64	7.97	7.22	7.65	7.43
9	DON	0.86	2.60	2.50	1.70	1.50	0.86	0.39
	PON	0.67	1.30	0.50	0.40	0.90	0.45	0.15
	TON	1.53	3.70	3.00	2.10	2.40	1.31	0.54
	NH_4^+-N	12.3	11.2	12.6	1.52	0.01	0.04	0.01
	NO_2^--N	0.55	0.80	0.67	0.70	0.003	0.013	0.005
	NO_3^--N	2.25	2.10	2.67	14.8	15.5	15.4	15.33
	Total N	16.63	17.76	18.94	19.22	17.90	16.76	15.88

Table 4. Changes of Nitrogen Compound Concentrations in mg N/ℓ at 18° C for Water Samples from the Slnava Reservoir. Sampling dated 26.IV.80.

Experiment numbers	Nitrogen fractions	Period of Incubation						
		0	7	21	28	35	43	50
10	DON	1.26	1.63	1.37	1.06	0.28	0.41	-
	PON	0.90	0.35	0.15	0.16	0.17	0.19	-
	TON	2.16	1.96	1.52	1.22	0.45	0.60	-
	NH_4^+-N	0.34	0.36	0.005	0.005	0.005	0.005	-
	NO_2^--N	0.03	0.17	0.002	0.010	0.005	0.002	-
	NO_3^--N	2.13	2.12	3.13	3.39	4.67	4.56	-
	Total N	4.67	4.63	4.66	4.62	5.12	5.16	-
11	DON	1.38	0.76	0.94	0.47	0.44	0.38	-
	PON	2.45	2.27	1.71	0.24	0.07	0.20	-
	TON	3.83	3.03	2.65	0.71	0.51	0.58	-
	NH_4^+-N	4.73	3.94	0.02	0.005	0.005	0.005	-
	NO_2^--N	0.15	0.79	0.002	0.002	0.002	0.002	-
	NO_3^--N	2.20	2.95	7.22	10.18	10.15	10.35	-
	Total N	10.91	10.71	9.90	10.89	10.66	10.93	-
12	DON	2.24	1.59	2.34	0.70	1.07	1.06	1.43
	PON	3.06	2.92	3.58	0.86	0.59	0.69	0.48
	TON	5.30	4.51	5.92	1.56	1.66	1.75	1.91
	NH_4^+-N	14.82	15.69	1.55	1.78	1.52	1.64	1.78
	NO_2^--N	0.72	1.34	0.02	0.04	0.005	0.005	0.005
	NO_3^--N	2.53	4.39	15.99	18.45	18.63	18.83	18.96
	Total N	23.37	25.93	23.48	21.83	21.81	22.22	22.65

For instance, by comparing the experimental results obtained in April, the nitrite-N peak was reached at the 7th day in water samples with total nitrogen content adjusted to 10 or 23 mg/ℓ and with control sample having 4.6 mg N/ℓ. It seems that the various levels of total nitrogen in the system have only a limited influence on the initial rate of ammonium-N oxidation. From this it can be concluded that the nitrification capacity of our experimental systems is sufficient for all of the tested concentration levels of mineral nitrogen forms.

For comparison, experiments were made in April at 12° C, as is shown in Table 2. By comparing the results obtained at 12° C with those at 18° C it is clearly visible that a slower rate of nitrification is obtained at the lower temperature. The nitrite-N peak was achieved at the 13th day of experiment and the ammonium-N decrease was finished only at the 34th day in 12° C experiment.

The organic nitrogen content during all of our experiments was rather unstable. With water samples taken from the reservoir in February or April the total organic nitrogen concentration was considerably decreased by the end of the experiments. In practically all cases we have observed a direct connection between the decrease of the total and particular organic nitrogen. It seems that the interpretation of this trend lies in the losses of some part of the nitrogen bound to microorganism biomasses by sedimentation because of the ability of bacteria to be immobilized on solid surfaces. This nitrogen quota can not be taken into account quantitatively during sampling and the result is lowered levels of individual nitrogen function as well as total nitrogen. This methodological error leads to some

deviation in the sum of total nitrogen contents in the experimental systems. Anyway these deviations do not exceed ± 15% of the arithmetical mean. So the given systems may be considered as virtually closed systems and the exchange of nitrogen through air-water interface may be assumed to be negligible.

On the basis of a preliminary analysis of the experimental results it is possible to conclude that the water from the Slnava Reservoir has the ability to support nitrification in different seasons. The quantitative assessment of the nitrifying ability may be accomplished only when the data from the microbiological and biological analyses of the water samples are available. When these data are absent one way to estimate the nitrification activity in the water is by the use of mathematical modeling.

Model of Nitrogen Transformation

Mathematical models for the nitrogen cycle in water have been considered by many authors. The theoretical approaches to mathematical modeling of nitrogen transformation processes have been discussed by Leonov (1980). Examples of applying the mathematical models to analyze the nitrogen cycle, or only a part of it, are presented: (i) for experimental systems by Knowles et al., (1965) and Leonov and Ajzatullin (1978); (ii) for activated sludge systems by Poduska and Andrews (1975) and Beck et al. (1979); (iii) for estuary ecosystems by Thomann et al., (1971) and Najarian and Harleman (1977); (iv) for river ecosystems by Shima et al., (1978), Knowles and Wakeford (1978), Casapieri et al., (1978), Miller and Jennings (1979), (v) for lake and reservoir ecosystems by Anderson et al., (1976).

The mathematical model described in the present report is based on the previous study by Leonov (1980). Because the model is intended to be used for analysis of the dynamics of the nitrogen compounds in experimental dark conditions, i.e., without photosynthetic production of organic matter, the following assumptions have been made:

(i) the model must include the main nitrogen compounds measured in the experiments, such as ammonium-N (NH_4^+-N), nitrite-N (NO_2^--N), nitrate-N (NO_3^--N), dissolved organic-N (DON) and particulate organic-N (PON);

(ii) in the given model PON is subdivided into the fractions such as detritus-N (N_D) and organically bound nitrogen in microorganism biomasses - Nitrosomonas (B_1), Nitrobacter (B_2), heterotrophs (B_3) and phytoplankton (PL);

(iii) the following ecological processes are considered to be important in the nitrogen transformations under dark (non-photosynthetic) conditions:

(a) growth of heterotrophs transforming DON to NH_4^+-N;

(b) growth of Nitrosomonas transforming NH_4^+-N to NO_2^--N;

(c) growth of Nitrobacter transforming NO_2^--N to NO_3^--N;

(d) the decomposition of organic-N bound to the phytoplankton biomass;

(e) the formation of detritus-N and its decomposition to DON.

(iv) the model should take into account the general functions of microorganisms, i.e., the uptake of nutrients, the excretion of metabolites and non-predated mortality; these functions are considered to be important for an ecological explanation of nitrogen transformations in a water environment;

(v) the bacterial uptake of nutrients is described by Longmuir-Hinshelwood equations, where the uptake rate is a function of water temperature and nutrient concentration;

(vi) the uptake rate of nutrients by phytoplankton is described as function of temperature and nutrient contents in the water and the phytoplankton cells;

(vii) phytoplankton can take up the mineral and organic nitrogen compounds as an interchangeable food source with preferences so that the metabolism of each nitrogen source occurs simultaneously and interdependently;

(viii) the rates of metabolite excretion by microorganisms are given by functions of specific uptake rates with excretion activities that are different for each type of microorganism;

(ix) the rate of detritus decomposition to DON is a function of temperature and in its simplest form this process may be described by first order chemical kinetics;

(x) oxygen is also introduced in the model as an important water quality characteristic dependent on the nitrogen transformation.

Figure 2 illustrates the interrelationships between the compartments considered in the given model. The structure of the equations of the nitrogen transformation model is shown in Table 5. A detailed explanation of the model equations is presented elsewhere (Leonov, 1980).

Simulation of the Nitrogen Transformation

The mathematical model for nitrogen transformation presented above was used to describe the dynamics of the nitrogen fractions observed in the experiments with water from the Slnava Reservoir.

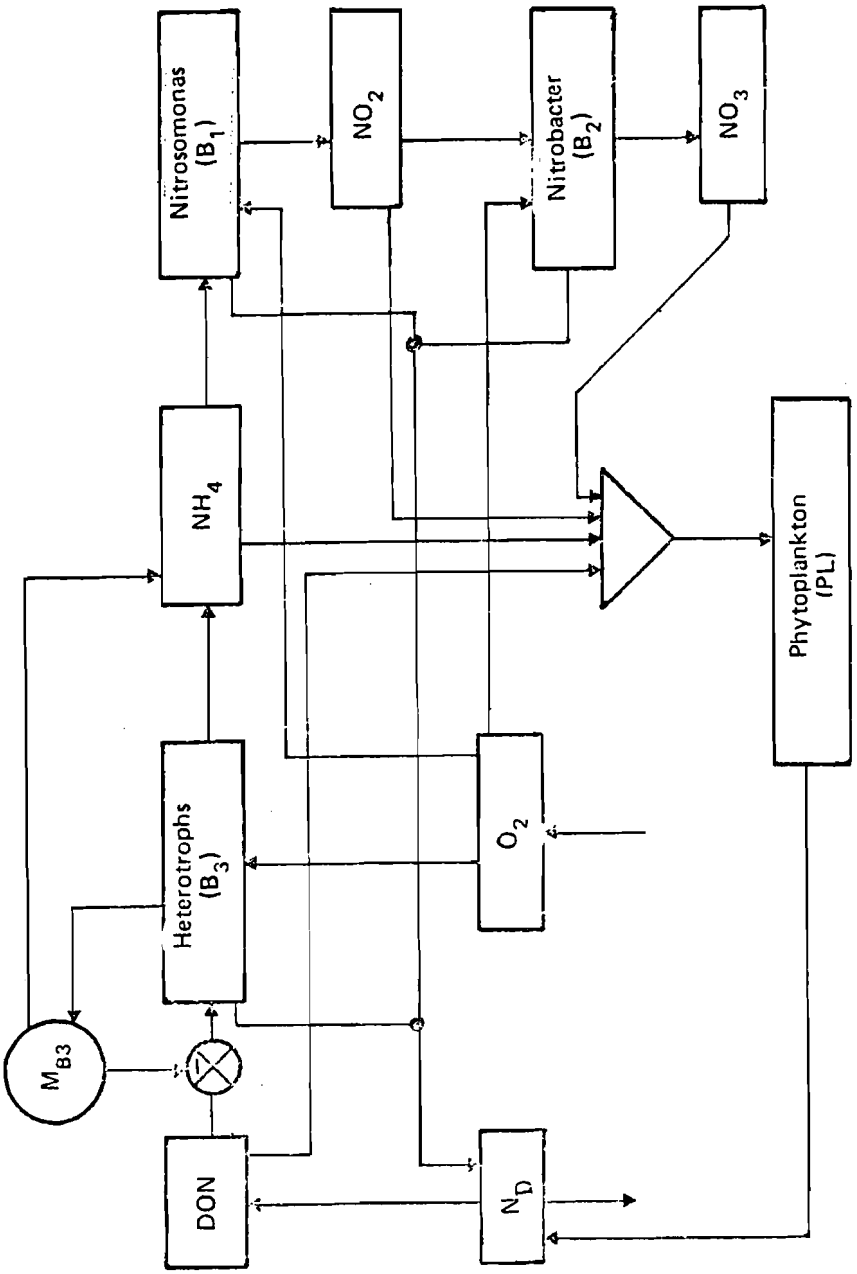

Figure 2. Components of the Nitrogen Transformation Model and their Interrelationships

Table 5. Mass Balance Equations for Nitrogen Transformation Model

Constituents	Symbol	Equations
1. Nitrosomonas-N (mgN/ℓ)	B_1	$\frac{dB_1}{dt} = (UP_{B1} - L_{B1} - S_{B1}) \cdot B_1$ *net growth* $UP_{B1} = \frac{K_1 \cdot R_{TB1} \cdot NH_4}{1 + G_1 \cdot NH_4}$ $L_{B1} = r_{B1} \cdot UP_{B1}$ $r_{B1} = \frac{a_1 \cdot UP_{B1}}{1 + a_2 \cdot UP_{B1}} + (1 - a_1/a_2)$ $S_{B1} = G_5 + G_6 \cdot r_{B1}$
2. Nitrobacter-N (mgN/ℓ)	B_2	$\frac{dB_2}{dt} = (UP_{B2} - L_{B2} - S_{B2}) \cdot B_2$ *net growth* $UP_{B2} = \frac{K_2 \cdot R_{TB2} \cdot NO_2}{1 + G_2 \cdot NO_2}$ $L_{B2} = r_{B2} \cdot UP_{B2}$ $r_{B2} = \frac{a_3 \cdot UP_{B2}}{1 + a_4 \cdot UP_{B2}} + (1 - a_3/a_4)$

Table 5. contd..

Constituents	Symbol	Equations
		$S_{B2} = G_7 + G_8 \cdot r_{B2}$
3. Heterotrophs-N (mgN/ℓ)	B_3	$\frac{dB_3}{dt} = (UP_{B3} - L_{B3} - S_{B3}) \cdot B_3$ (*net growth*) $UP_{B3} = \frac{K_3 \cdot R_{TB3} \cdot DON}{(1+G_3 \cdot DON) \cdot (1+G_4 \cdot M_{B3})}$ $L_{B3} = r_{B3} \cdot UP_{B3}$ $r_{B3} = \frac{a_5 \cdot UP_{B3}}{1+a_6 \cdot UP_{B3}} + (1 - a_5/a_6)$ $S_{B3} = G_9 + G_{10} \cdot r_{B3}$
4. Phytoplankton-N (mgN/ℓ)	PL	$\frac{dPL}{dt} = (UP_F - L_F - S_F) \cdot PL$ (*net growth*) $UP_F = \frac{K_4 \cdot R_{TF}}{1 + PL/PoolN}$ $PoolN = d_1 \cdot NH_4 + d_2 \cdot NO_2 + d_3 \cdot NO_3 + d_4 \cdot DON$ $L_F = r_F \cdot UP_F$

Table 5. contd..

Constituents	Symbol	Equations
		$r_F = \frac{a_7 \cdot UP_F}{1+a_8 \cdot UP_F} + (1 - a_7/a_8)$ $S_F = G_{11} + G_{12} \cdot r_F$
5. Dissolved organic-N (mgN/ℓ)	DON	$\frac{dDON}{dt} = K_5 \cdot N_D + L_F \cdot PL - P_{FDON} \cdot PL - UP_{B3} \cdot B_3$ *detritus decay* ; *excretion by phytoplankton* ; *uptake by phytoplankton* ; *uptake by heterotrophs*
6. Ammonium-N (mgN/ℓ)	NH_4	$\frac{dNH_4}{dt} = q_1 \cdot L_{B3} \cdot B_3 - UP_{B1} \cdot B_1 - P_{FNH_4} \cdot PL + K_6 \cdot M_{B3}$ *excretion by heterotrophs* ; *uptake by Nitrosomonas* ; *uptake by phytoplankton* ; *metabolite decay*
7. Nitrite-N (mgN/ℓ)	NO_2	$\frac{dNO_2}{dt} = L_{B1} \cdot B_1 - UP_{B2} \cdot B_2 - P_{FNO_2} \cdot PL$ *excretion by Nitrosomonas* ; *uptake by Nitrobacter* ; *uptake by phytoplankton*

Table 5. contd..

Constituents	Symbol	Equations
8. Nitrate-N (mgN/ℓ)	NO_3	$\frac{dNO_3}{dt} = L_{B2} \cdot B_2$ *excretion by Nitrobacter* $- P_{FNO_3} \cdot PL$ *uptake by phytoplankton*
9. Non-living organic-N (mgN/ℓ)	N_D	$\frac{dN_D}{dt} = S_{B1} \cdot B_1$ *mortality of Nitrosomonas* $+ S_{B2} \cdot B_2$ *mortality of Nitrobacter* $+ S_{B3} \cdot B_3$ *mortality of heterotrophs* $+ S_F \cdot PL$ *mortality of phytoplankton* $- K_5 \cdot N_D$ *decay* $- K_7 \cdot N_D$ *sedimentation*
10. Specific metabolite of Heterotrophs (mgN/ℓ)	M_{B3}	$\frac{dM_{B3}}{dt} = (1 - q_1) \cdot L_{B3} \cdot B_3$ *excretion by heterotrophs* $- K_6 \cdot M_{B3}$ *decomposition*
11. Dissolved oxygen ($mgO_2/ℓ$)	O_2	$\frac{dO_2}{dt} = K_{re} \cdot (O_2^{sat} - O_2)$ *reaeration* $- q_2 \cdot L_F \cdot PL$ *respiration of phytoplankton* $- q_3 \cdot L_{B3} \cdot B_3$ *respiration of heterotrophs* $- q_4 \cdot L_{B1} \cdot B_1$ *respiration of Nitrosomonas* $- q_5 \cdot L_{B2} \cdot B_2$ *respiration of Nitrobacter*

Table 5. contd..

Constituents	Symbol	Equations
Temperature-dependent parameters:		
1. Temperature reduction factor for uptake rate of nitrifiers (unitless)	R_{TB1} R_{TB2}	$R_{TB1}=R_{TB2}=\frac{0.0759\cdot(e^{0.247\cdot T}-1)}{1+0.0759\cdot e^{0.247\cdot T}}$
2. Temperature reduction factor for uptake rate of heterotrophs (unitless)	R_{TB3}	$R_{TB3}=0.08+\frac{0.0316\cdot(e^{0.326\cdot T}-1)}{1+0.034\cdot e^{0.326\cdot T}}-\frac{3.39\cdot10^{-5}\cdot(e^{0.304\cdot T}-1)}{1+3.39.10^{-5}\cdot e^{0.304\cdot T}}$
3. Temperature-reduction factor for uptake rate of phytoplankton (unitless)	R_{TF}	$R_{TF}=\frac{0.009\cdot(e^{0.288\cdot T}-1)}{1+0.009\cdot e^{0.288\cdot T}}$
4. Decomposition rate of N_D to DON (day^{-1})	K_5	$K_5=\frac{4.15\cdot10^{-4}\cdot(e^{0.463\cdot T}-1)}{1+4.15\cdot10^{-4}\cdot e^{0.463\cdot T}}$
5. Decomposition rate of M_{B3} (day^{-1})	K_6	$K_6=K_{6(20^o)}\cdot1.05^{(T-20)}$
6. Sedimentation rate (day^{-1})	K_7	$K_7=K_{7(20^o)}\cdot1.05^{(T-20)}$
7. Reaeration rate (day^{-1})	K_{re}	$K_{re}=K_8\cdot1.05^{(T-20)}$

Table 5. contd..

Constituents	Symbol	Equations
8. Saturation level of oxygen (mgO_2/ℓ)	O_2^{sat}	$O_2^{sat} = 14.61996 - 0.4042 \cdot T + 0.00842 \cdot T^2 - 0.00009 \cdot T^3$ where T is water temperature (in ^{o}C) in range 0 - $30^{o}C$
Uptake rate of nutrients by phytoplankton (day^{-1})	P_{FN}	$P_{FN} = \frac{K_4 \cdot R_{TF} \cdot d_i \cdot N}{PoolN + PL}$ where i for d is changed from 1 to 4 when N = NH_4, NO_2, NO_3 and DON, respectively.

The following are terms not defined earlier:

UP_{B1}, UP_{B2}, UP_{B3} and UP_F are the specific uptake rates of nutrients by Nitrosomonas, Nitrobacter, heterotrophs and phytoplankton, respectively (all day^{-1});

L_{B1}, L_{B2}, L_{B3} and L_F are specific rates of metabolite excretions of the same microorganisms (all day^{-1});

r_{B1}, r_{B2}, r_{B3} and r_F are excretion activities of the same microorganisms (all unitless);

S_{B1}, S_{B2}, S_{B3} and S_F are non-predated mortality of the same microorganisms (all day^{-1});

K_1, K_2, K_3 and K_4 are maximum uptake rates of nutrients by the same microorganisms, all $(mg/\ell)^{-1} \cdot (day)^{-1}$;

Table 5. contd...

K_8 is the reaeration rate constant (day^{-1});

G_1, G_2, G_3 and G_4 are coefficients showing limits of uptake rate by nutrient contents, all $(mg/\ell)^{-1}$;

G_{5-12} are coefficients determining the mortality of microorganisms;

a_i are coefficients regulating the excretion activities of microorganisms (all unitless);

d_i are preference coefficients for the metabolism of nutrient sources by phytoplankton (all unitless);

q_1 is a factor indicating the proportion of waste products in heterotrophic metabolism (unitless);

q_{2-5} are stoicheometric coefficients for calculating oxygen consumption in the processes of nitrogen transformation by microorganisms (mgO_2/mgN).

Table 6 shows the initial concentrations of the nitrogenous compounds taken from the experimental data (Tables 1-4) as well as the values of the rate coefficients used in the model. The ranges in the initial concentration changes of chemical nitrogen forms, DON, NH_4^+-N and NO_3^--N in the experiments are 0.71-2.24, 0.3-30.3, 0.014-0.55, and 0.049-2.53 mg N/ℓ, respectively.

Because there are many methodological difficulties in differentiating various strains of microorganisms involved in nitrogen transformation and to evaluate their biomasses, the initial values of nitrogen bound in the particulate nitrogen fractions, detritus and biomasses of microorganisms were not determined experimentally. For the simulation runs these initial concentrations were evaluated using the reasonable assumption that the major part of particulate nitrogen, i.e., about 90%, is included in non-living particulate matter or detritus, and only small quota (less than 10%) is bound in the biomasses of viable microorganisms. From a quantitative point of view the amount of nitrogen bound to the biomasses of bacteria, nitrifiers, and heterotrophs, is very low (Ruban, 1961). For example, the estimated order of biomass of nitrifying bacteria in units of nitrogen is about 10^{-3}-10^{-4} mg N/ℓ (Curtis et al., 1975). Thus the assumptions used give for different simulation runs ranges in the values of particulate nitrogen fractions of about 0.6-2.96 mg N/ℓ (for detritus), $(0.7\text{-}3.5)\cdot 10^{-3}$ mg N/ℓ (for Nitrosomonas), $(0.8\text{-}2)\cdot 10^{-3}$ mg N/ℓ (for Nitrobacter), $(8\text{-}8.5)\cdot 10^{-5}$ mg N/ℓ (for heterotrophs) and 0.07-0.1 mg N/ℓ (for phytoplankton).

Table 6. Initial Concentrations of Nitrogen Compounds and Rate Constants used for Simulating the Nitrogen Transformations in Slnava Reservoir Water (to Figures 3-14)

Date of water sampling		24.X.79						11.II.80			26.IV.80		
Temperature, °C		18			12			18			18		
Experiment numbers		1	2	3	4	5	6	7	8	9	10	11	12
variables, mg/ℓ	DON	0.71	0.71	0.71	0.71	0.71	0.71	0.86	0.86	0.86	1.26	1.38	2.24
	NH_4^+-N	1.8	4.35	30.3	1.8	4.44	25.7	0.3	3.2	12.3	0.34	4.73	14.82
	NO_2^--N	0.021	0.072	0.34	0.027	0.086	0.37	0.014	0.147	0.55	0.03	0.15	0.72
	NO_3^--N	0.049	0.4	1.15	0.073	0.26	1.57	1.09	2.13	2.25	2.13	2.2	2.53
	N_D	0.83	0.83	0.83	0.83	0.83	0.83	0.6	0.6	0.6	0.8	2.35	2.96
	B_1	$7 \cdot 10^{-4}$	$7 \cdot 10^{-4}$	$7 \cdot 10^{-4}$	$7 \cdot 10^{-4}$	$7 \cdot 10^{-4}$	$7 \cdot 10^{-4}$	0.0035	0.0035	0.0035	0.0036	0.0036	0.0036
	B_2	$8 \cdot 10^{-4}$	$8 \cdot 10^{-4}$	$8 \cdot 10^{-4}$	$8 \cdot 10^{-4}$	$8 \cdot 10^{-4}$	$8 \cdot 10^{-4}$	0.002	0.002	0.002	0.0022	0.0022	0.0022
	B_3	$8 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$8.5 \cdot 10^{-5}$	$8.5 \cdot 10^{-5}$	$8.5 \cdot 10^{-5}$
	M_{B3}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	PL	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.1	0.1	0.1
	O_2	9.2	9.2	9.2	10.8	10.8	10.8	9.2	9.2	9.2	9.2	9.2	9.2
constants	K_1=12.8	K_5=0.63	a_1=0.5	a_5=0.0073	d_1=0.03	G_1=1.5	G_5=0.2	G_9=0.8	q_1=0.97	q_5=1.14			
	K_2=51.3	K_6=0.363	a_2=0.67	a_6=0.0182	d_2=0.006	G_2=2.0	G_6=0.0	G_{10}=0.4	q_2=13.35				
	K_3=18.4	K_7=0.0	a_3=1.0	a_7=0.2	d_3=0.003	G_3=0.14	G_7=0.15	G_{11}=0.3	q_3=13.35				
	K_4=0.92	K_8=1.25	a_4=1.39	a_8=0.202	d_4=0.0	G_4=700	G_8=0.0	G_{12}=0.0	q_4=3.42				

Note: temperature-dependent constants are presented for 18°C

In the model runs similar values of rate coefficients were used for the simulation of the dynamic behavior of the nitrogen fractions. The values for the rate coefficients were taken from the earlier report where the influence of different experimental conditions on nitrogen transformation was likewise studied with the use of a model (Leonov, 1980).

It is interesting to compare the values of the rate coefficients used for the description of bacterial growth in nitrogen transformation models. In Monod- (or Michaelis-Menten) type kinetics, which are most commonly used for modeling the bacterial growth, the main kinetic parameters are the maximum specific growth (or substrate uptake) rate (μ, day^{-1}) and the Michaelis saturation constant (K_M, mg N/ℓ). The yield coefficient, Y, is also an important parameter in models of bacteria growth, and Y shows which part of the utilized substrate is bound to bacterial biomass (Sherrard and Schoeder, 1973).

In the given model the bacterial biomass changes at each moment of time are defined by differences in the values of specific rates of substrate uptake, the excretion of metabolized product, and mortality. Therefore, for comparison of the rate coefficients used in this study and those available in the literature, we must couple the kinetic terms describing bacterial uptake and excretion. Thus, after rearranging the corresponding equations, presented in Table 5, the following expressions for μ and K_M may be formulated.

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

$$K_M = \frac{1}{G_k + a_{j+1} \cdot K_i} \quad , \tag{2}$$

where i=1, j=1 and k=1 for Nitrosomonas; i=2, j=3 and k=2 for Nitrobacter. For heterotrophs the form of equations (1) and (2) may be applied only for t=0 when $M_{B3} = 0$. For cases where $t \neq 0$, μ and K_M should be corrected by M_{B3} and equations for computing these coefficients may be written as

$$\mu = \frac{K_3 \cdot (a_5/a_6)}{G_3 + G_3 \cdot G_4 \cdot M_{B3} + a_6 \cdot K_3} \quad , \tag{3}$$

$$K_M = \frac{1 + G_4 \cdot M_{B3}}{G_3 + G_3 \cdot G_4 \cdot M_{B3} + a_6 \cdot K_3} \quad . \tag{4}$$

The values of the yield coefficients, Y, which in mathematical models of bacterial growth are commonly used as constant values, may be calculated here for each type of bacteria through the excretion activities (r_{Bi}). Thus in the given model Y is a variable parameter that may be estimated by a simple expression:

$$Y_i = 1 - r_{Bi} \quad , \tag{5}$$

where i=1, 2 and 3 for Nitrosomonas, Nitrobacter and heterotrophs. For each type of bacteria and for individual stages of bacterial growth Y will change its value in accordance with the conditions for growth.

Table 7 presents the set of kinetic coefficient values used in practice for modeling the bacterial growth. It shows also the initial concentrations of bacterial biomasses in mg N/ℓ used in modeling the nitrogen transformations and it confirms that the levels of bacterial biomasses applied in this study, as in earlier studies of nitrogen transformation in different water environments (Leonov, 1980), correspond well to those evaluated for natural situations (Curtis, et al., 1975). The rate

Table 7. Review of Rate Coefficients used for Description of Bacterial Growth in Nitrogen Transformation Models

Authors of experimental observations	Type of water	Temperature °C	Mathematical modeling					
			Bacteria	Initial bacterial biomass, mgN/ℓ	K_M mgN/ℓ	μ day^{-1}	Y	Reference
Knowles et. al.,1965	River water	18-19	Nitrosomonas	0.02-0.1	0.2-8.0	0.2-2.1	0.05	Knowles et. al.,1965
			Nitrobacter	0.01-0.1	0.2-8.0	0.5-2.5	0.01	
			Nitrosomonas	0.05	0.06	0.7-1.2	0.05	Harleman, 1978
			Nitrobacter	0.02	1.7	1.1-1.8	0.02	
			Nitrosomonas	0.0015	0.066	1.11	0.01-0.64	Leonov,1980
			Nitrobacter	0.008	0.026	0.517	0.03-0.58	
			Heterotrophs	0.04	0.17-0.19	1.09-2.89	0.38-0.39	
Poduska and Andrews, 1975	Sewage	23 ± 1	Nitrosomonas	6.1	0.063	1.08	0.05	Poduska and Andrews,1975
			Nitrobacter	5.5	0.160	1.44	0.02	
-	River water	-	Nitrifiers	0.01	10.0	0.08	1.0	Shima et.al. 1978
			Heterotrophs	10.0	100.0	0.4	0.5	
Beck et.al. 1978	Sewage	10-15	Nitrosomonas	5.0	2.5	0.72	0.041	Beck,1979
			Nitrobacter	3.0	1.2	0.93	0.033	
Brand and Rakestraw, 1941	Sea water	18-19	Nitrosomonas	$5\cdot10^{-7}$	0.002	0.495	0.03-0.3	Leonov,1980
			Nitrobacter	$3\cdot10^{-8}$	0.002	0.497	0.03-0.93	
			Heterotrophs	$1\cdot10^{-4}$	0.091-0.145	2.47-2.55	0.13-0.3	
Votintsev, 1948	Lake water	18-19	Nitrosomonas	$4\cdot10^{-4}$	0.6	1.2	0.05	Harleman, 1978
			Nitrobacter	$7\cdot10^{-3}$	1.7	1.8	0.02	
			Heterotrophs	$1\cdot10^{-4}$	0.15	1.0	0.2	
			Nitrosomonas	$7\cdot10^{-4}$	0.021-0.058	0.38-0.4	0.06-0.77	Leonov,1980
			Nitrobacter	$(8-8.5)\cdot10^{-3}$	0.04-0.076	0.27-0.28	0.24-0.93	
			Heterotrophs	$8\cdot10^{-5}$	0.17-2.58	2.85-14.1	0.19-0.75	
DeMarco et. al.,1967	Sewage	18-19	Nitrosomonas	0.065	0.053	0.425	0.03-0.48	Leonov,1980
			Nitrobacter	0.5	0.035	0.305	0.08-0.41	
			Heterotrophs	0.04	0.2-0.78	0.92-0.96	0.68-0.69	
-	-	-	Nitrosomonas	-	0.06-5.6	0.46-2.2	0.03-0.13	Sharma and Ahlert,1977
			Nitrobacter	-	0.06-8.7	0.28-1.44	0.02-0.08	
			Heterotrophs	-	<1-181	7.2-17.0	0.37-0.79	
In the given report	Reservoir water	18	Nitrosomonas	$(0.7-3.5)\cdot10^{-3}$	0.099	0.95	0.11-0.71	In the given report
			Nitrobacter	$(0.8-2.0)\cdot10^{-3}$	0.014	0.503	0.02-0.52	
			Heterotrophs	$(8-8.5)\cdot10^{-4}$	2.105	15.54	0.37-0.39	
		12	Nitrosomonas	$7\cdot10^{-4}$	0.139	0.88	0.16-0.74	
			Nitrobacter	$8\cdot10^{-4}$	0.021	0.496	0.03-0.58	
			Heterotrophs	$8\cdot10^{-5}$	2.652	13.83	0.35-0.39	

coefficients, μ and K_M, also agree with the ranges of values quoted in the literature. As for the yield coefficient, Y, Table 7 shows the possible ranges of Y values in the different phases of bacterial growth as estimated by the given model in this study and previously (Leonov, 1980), these values are compared with constant values for Y available elsewhere in the literature.

Figures 3-14 show the agreement between the concentrations of nitrogen compounds observed in experiments and those calculated in the different simulation runs. From the analysis of these figures it appears that principally the model qualitatively describes the major tendencies in concentration changes of nitrogen forms measured in the experiments. From visual comparison of experimental and modeling results obtained for days of measurements (or water sampling) it is possible to derive some preliminary conclusions. Firstly, there is an unambiguous trend between the total nitrogen concentrations and the fitness of experimental and modeling data so that the best agreement is achieved at the lowest nitrogen concentrations while with increasing the nitrogen levels the more frequent deviations among experimentally measured and simulated nitrogen levels were observed. Secondly, the analysis of the nitrogen dynamics shows that the most differences could be found in the case of nitrite-N. It may be explained by the fact that in the nitrite dynamics there is a very short time period of its relatively high levels due to active phase of nitrification that define the difficulty in choosing the proper time step between measurements to find the nitrite-N dynamics. From the experimental results it is obvious that periods of nitrite-N increasing and

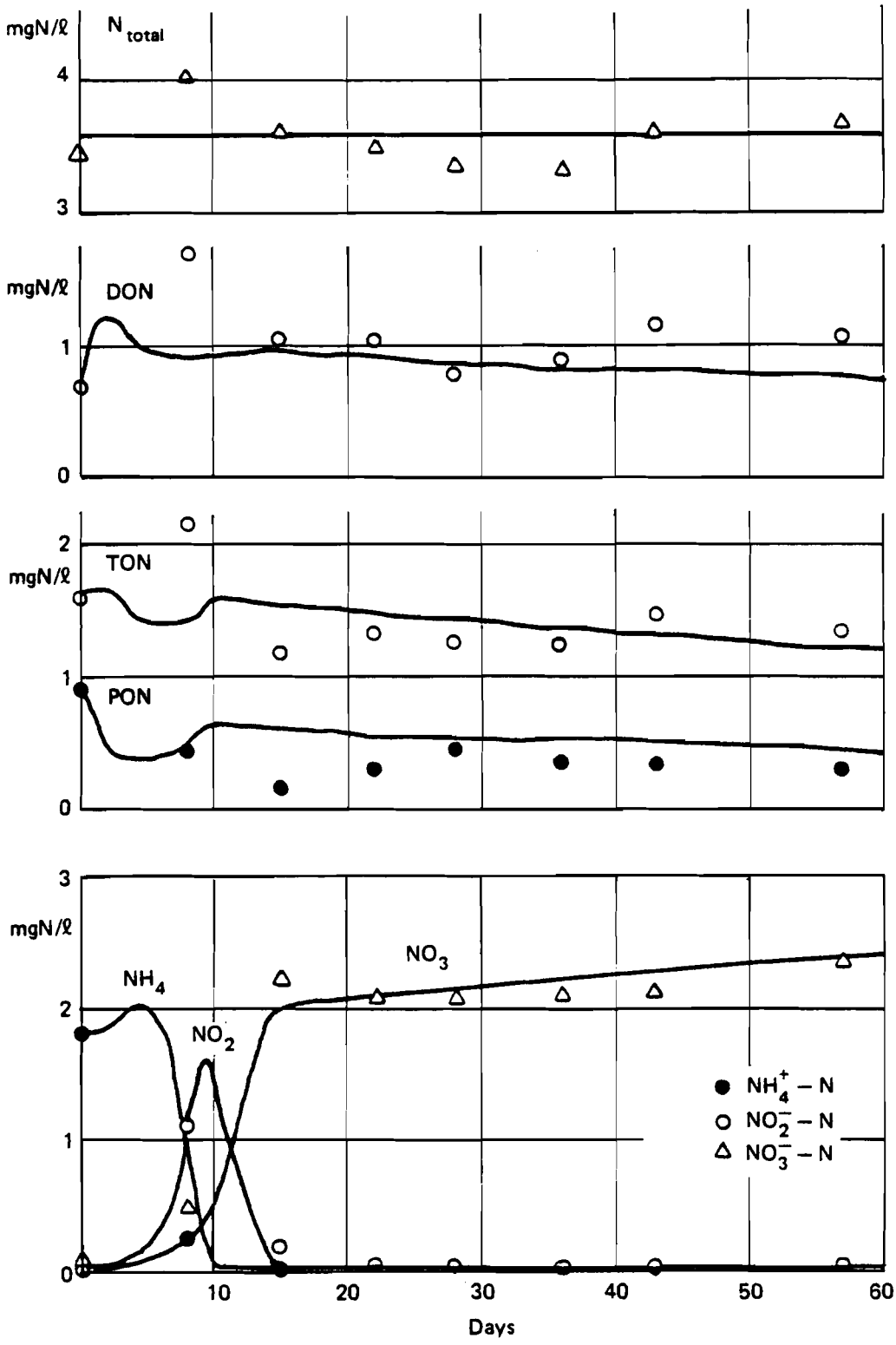

Figure 3. Comparison of Simulation Results (Curves) with Observations in Experiment 1 (Points)

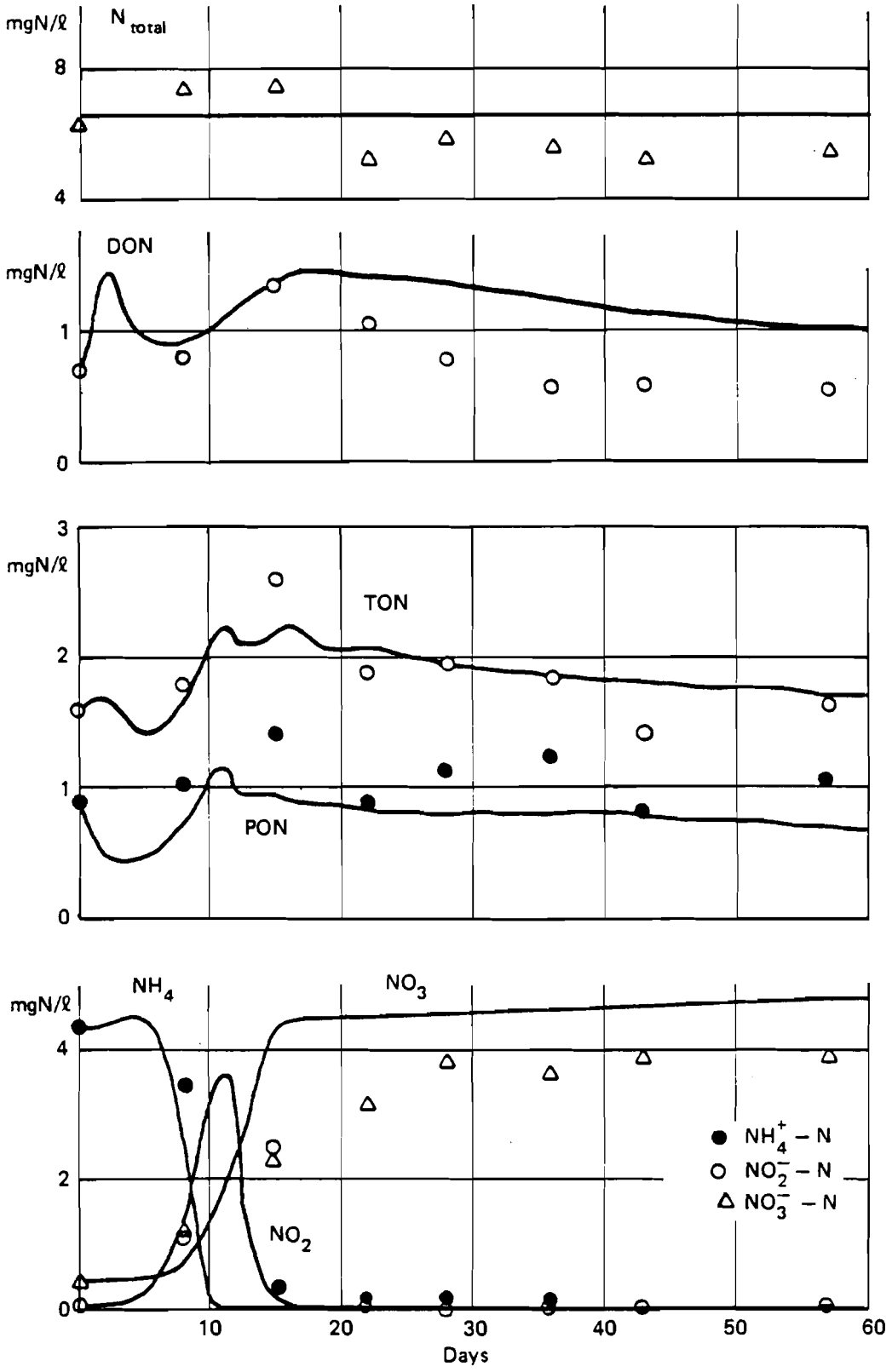

Figure 4. Comparison of Simulation Results (Curves) with Observations in Experiment 2 (Points)

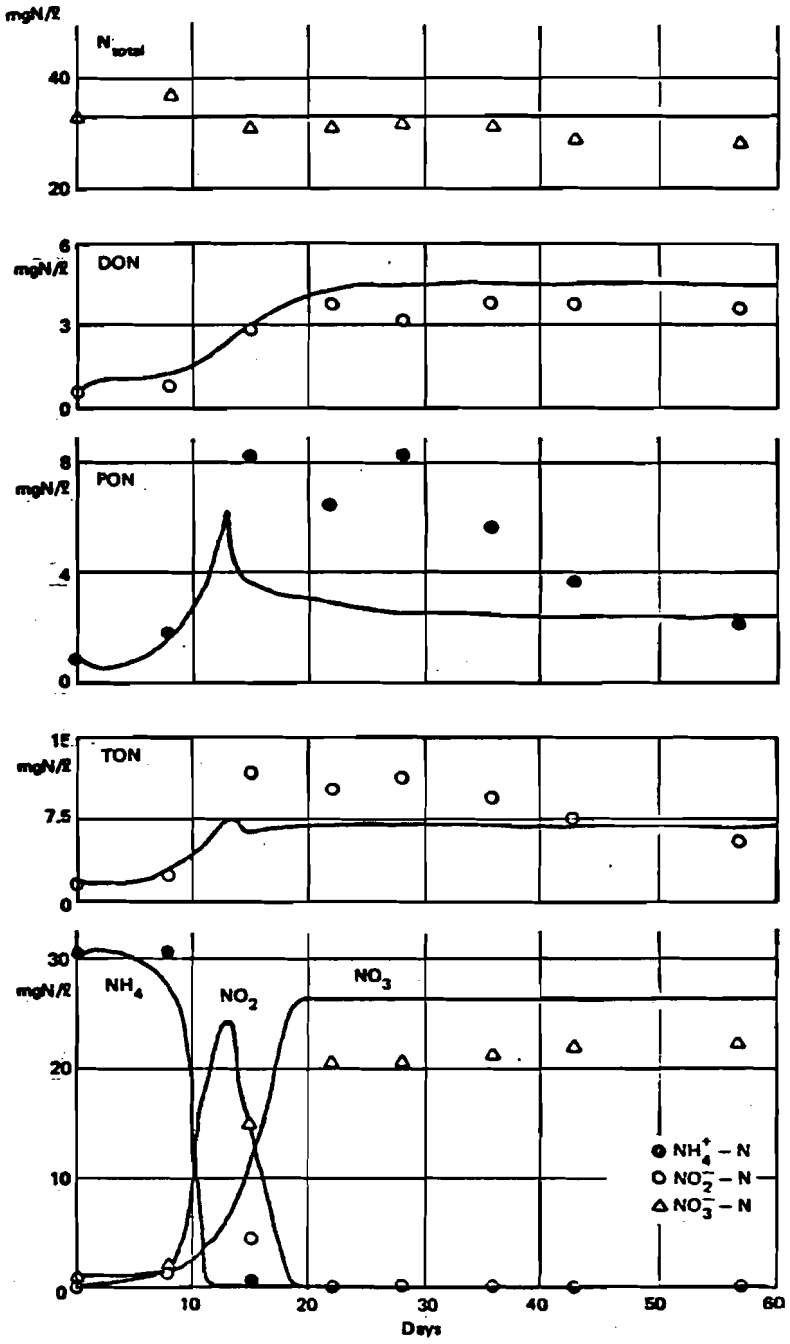

Figure 5. Comparison of Simulation Results (Curves) with Observations in Experiment 3 (Points)

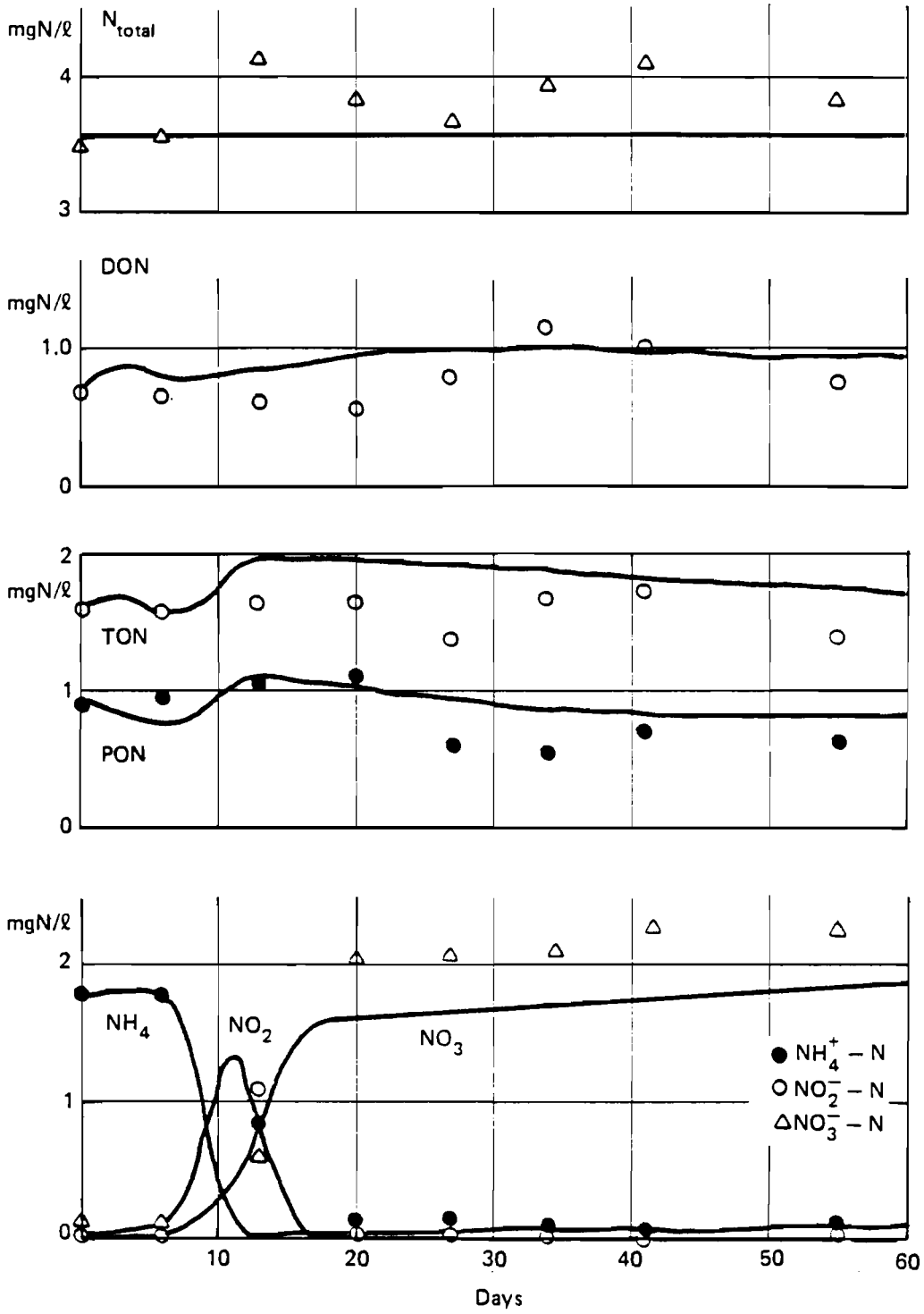

Figure 6. Comparison of Simulation Results (Curves) with Observations in Experiment 4 (Points)

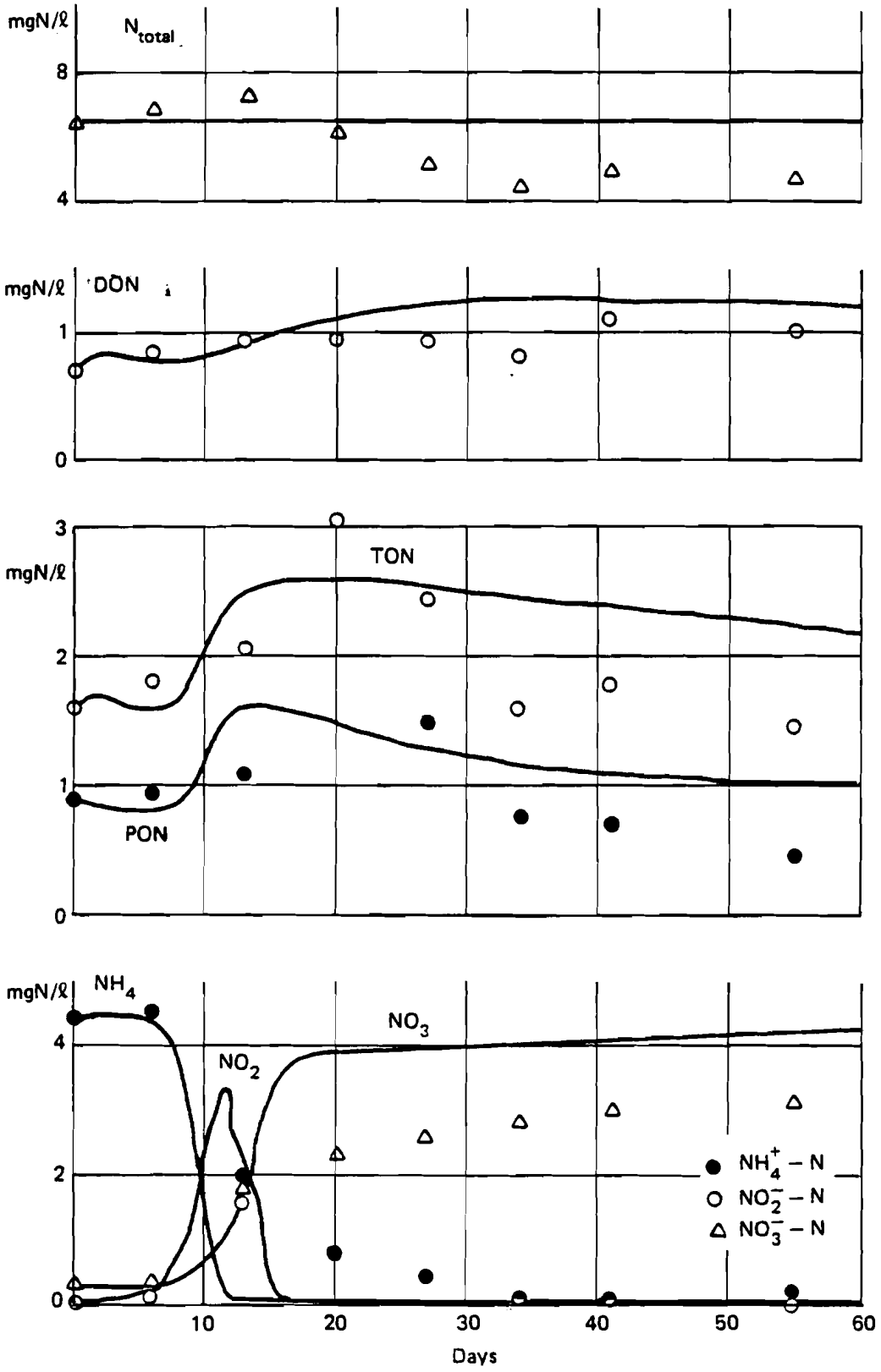

Figure 7. Comparison of Simulation Results (Curves) with Observations in Experiment 5 (Points)

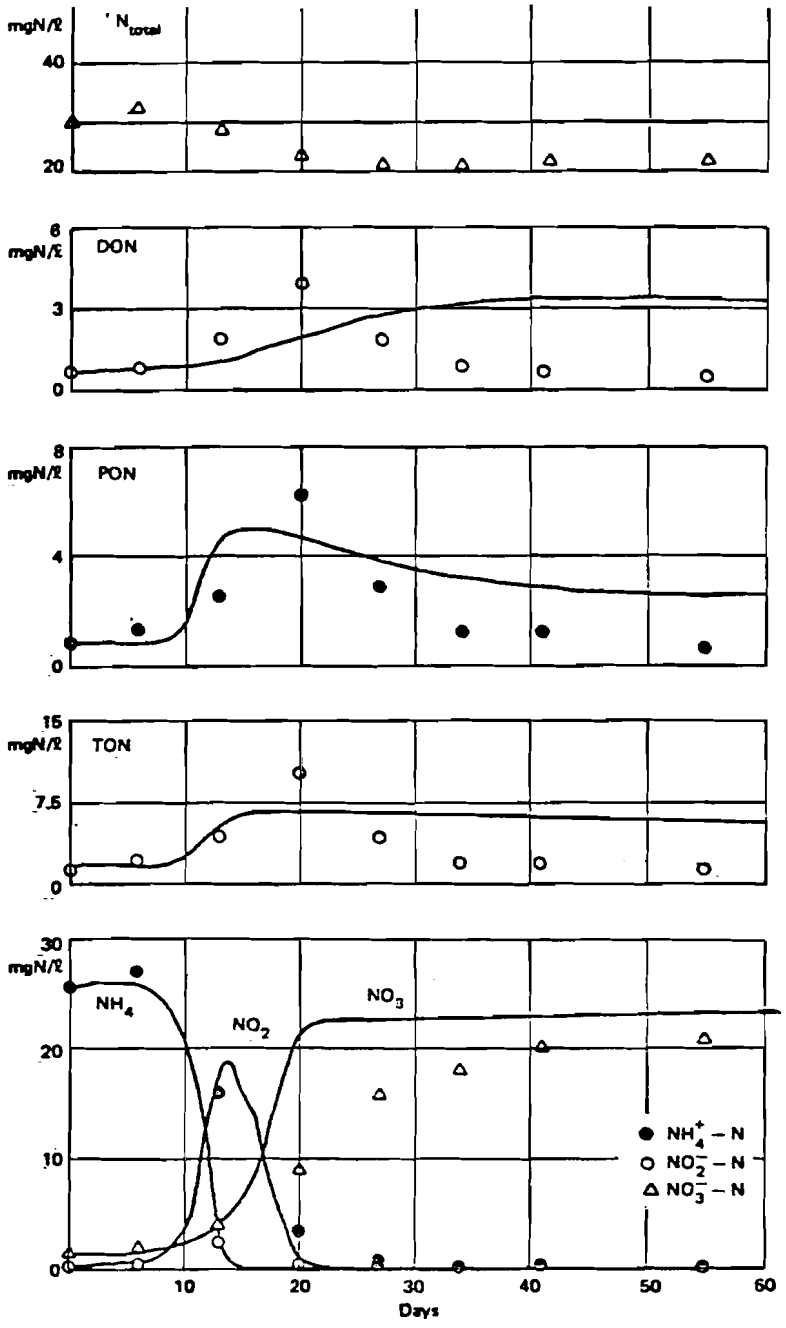

Figure 8. Comparison of Simulation Results (Curves) with Observations in Experiment 6 (Points)

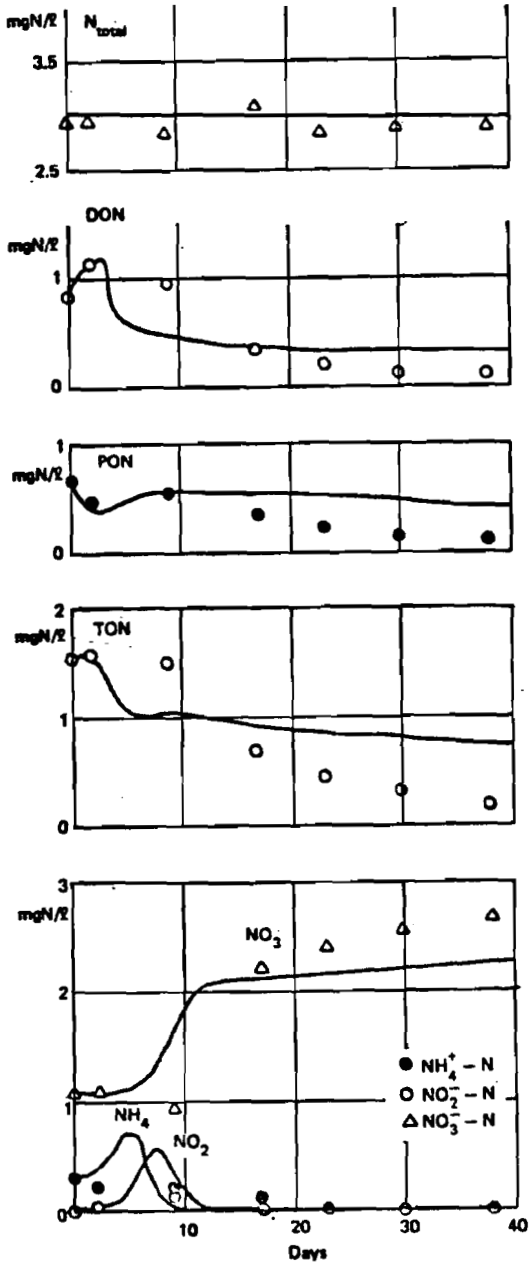

Figure 9. Comparison of Simulation Results (Curves) with Observations in Experiment 7 (Points)

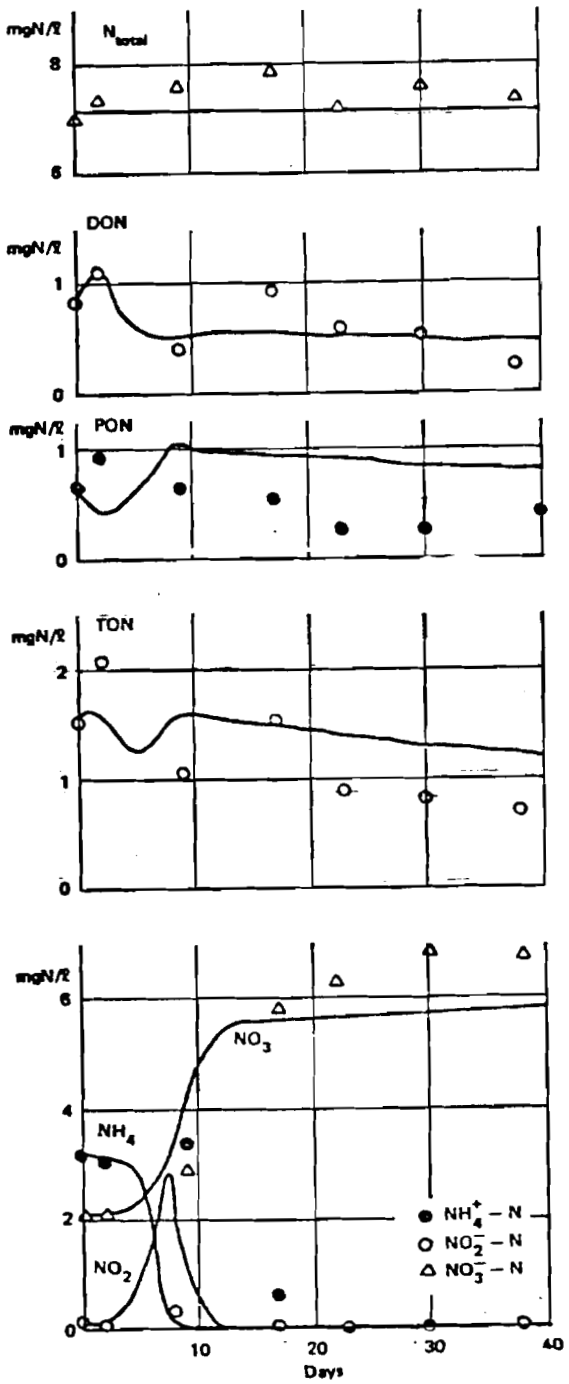

Figure 10. Comparison of Simulation Results (Curves) with Observations in Experiment 8 (Points)

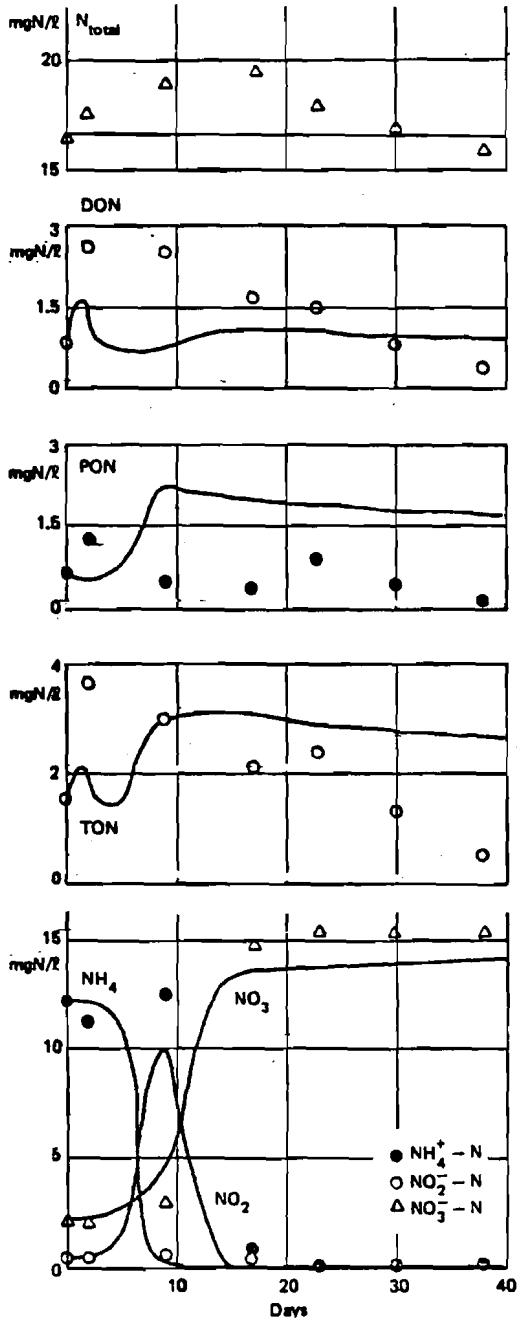

Figure 11. Comparison of Simulation Results (Curves) with Observations in Experiment 9 (Points)

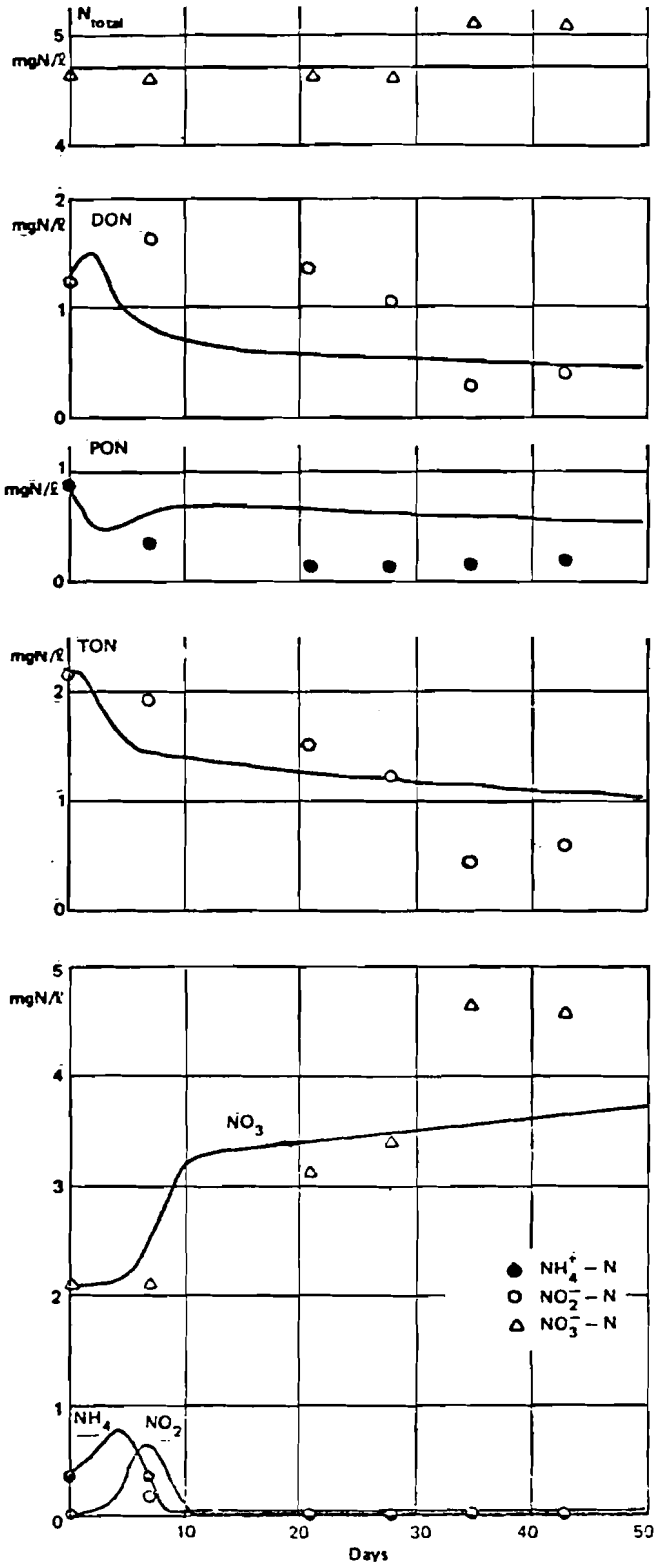

Figure 12. Comparison of Simulation Results (Curves) with Observations in Experiment 10 (Points)

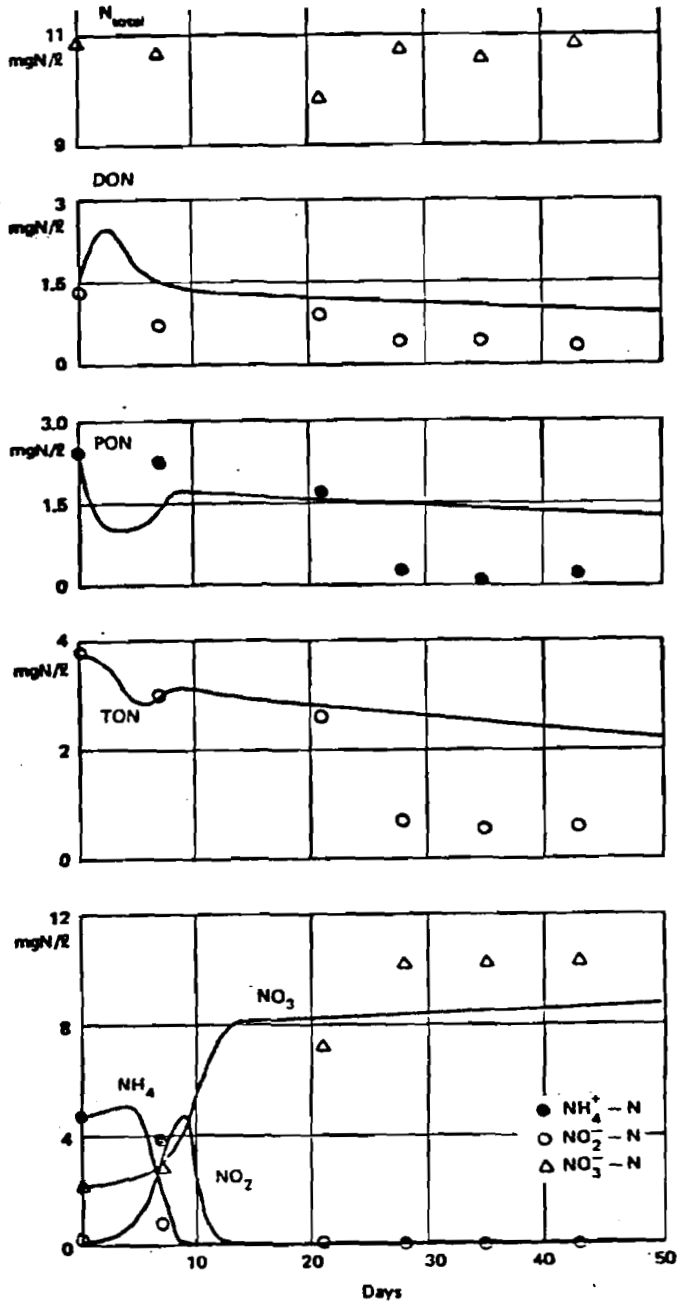

Figure 13. Comparison of Simulation Results (Curves) with Observations in Experiment 11 (Points)

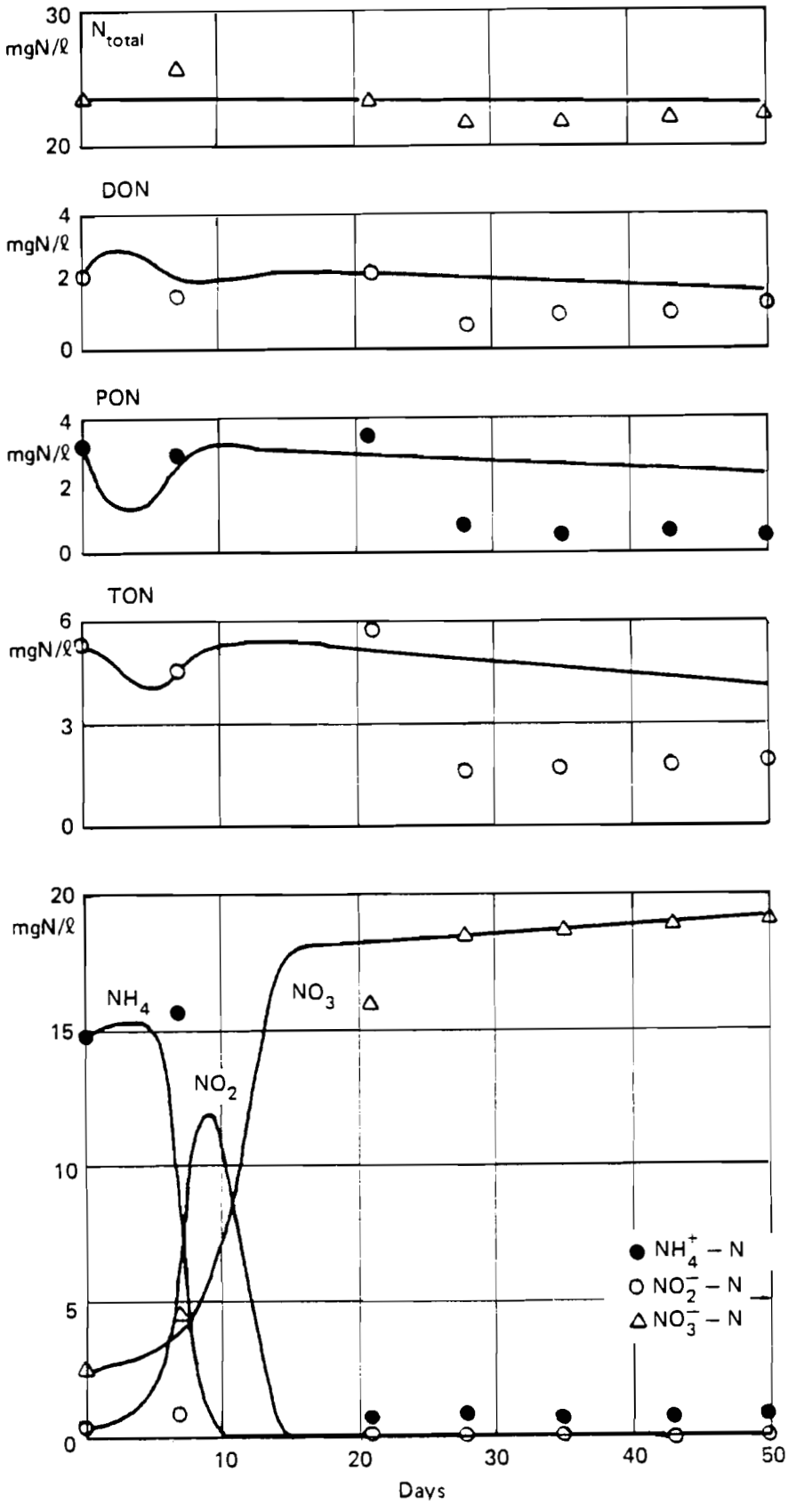

Figure 14. Comparison of Simulation Results (Curves) with Observations in Experiment 12 (Points)

its peaks were not detected by measurements and as a result of this the most part of experimentally measured nitrite-N concentrations are smaller than those obtained by modeling. Slightly higher experimental values in comparison with simulation results can be found for the ammonium-N and for the final levels of the nitrate-N as well as in a few cases for various forms of organic nitrogen. Finally it is possible to resume that in most cases there are no substantial differences between experimental and simulated results for other nitrogen forms such as DON, TON, and total N.

To obtain a quantitative assessment of how the modeling results agree with the observed nitrogen dynamics and to have some criteria showing that this agreement can not be attributed merely to chance, statistical methods should be applied. Thus, in analysis we will consider two groups of nitrogen compound concentrations or two samples derived for the experiments and the simulations. From the modeling results we will use only limited data to compare the concentrations of nitrogen compound at the same times or days as the measurements in the experiments.

The simplest criteria that may be used for comparison of samples, is the average (or the arithmetic mean). Table 8 shows the mean values for each of the nitrogen forms calculated on the basis of experimental measurements and simulation results. Within the limits of the accuracy of the analytical techniques of the measurements being used and the range of nitrogen variables measured and also the accuracy in the description of the nitrogen transformation by model, this Table consists a complete information about both data sets. In this sense the data in Table 8 on mean nitrogen concentrations are interesting only insofar

Table 8. Comparison of Mean Nitrogen Concentrations calculated on the basis of Measurements and Simulations and Survey of Model Errors

Nitrogen forms	Parameters	Numbers of experiments												Average values
		1	2	3	4	5	6	7	8	9	10	11	12	
DON	Observed mean	1.042	0.785	2.810	0.774	0.910	1.391	0.537	0.679	1.487	1.002	0.728	1.490	1.152
	Simulated mean	0.838	1.071	3.420	0.902	1.058	2.140	0.555	0.665	0.958	0.702	1.230	2.119	1.331
	Model errors	0.175	0.186	0.108	0.124	0.110	0.427	0.185	0.134	0.354	0.279	0.279	0.216	0.234
PON	Observed mean	0.400	1.056	4.682	0.805	1.054	2.157	0.360	0.553	0.624	0.320	1.157	1.740	1.284
	Simulated mean	0.576	0.774	2.337	0.898	1.168	2.905	0.508	0.794	1.522	0.635	1.612	2.629	1.374
	Model errors	0.214	0.183	0.403	0.114	0.178	0.245	0.230	0.314	0.535	0.341	0.295	0.311	0.330
TON	Observed mean	1.445	1.841	7.489	1.579	1.965	3.549	0.897	1.231	2.083	1.318	1.885	3.230	2.435
	Simulated mean	1.427	1.863	5.632	1.802	2.226	5.170	1.074	1.458	2.479	1.370	2.843	4.748	2.711
	Model errors	0.111	0.065	0.187	0.085	0.123	0.292	0.187	0.165	0.270	0.142	0.257	0.259	0.221
NH_4^+-N	Observed mean	0.273	1.072	7.716	0.640	1.561	9.228	0.134	1.476	5.383	0.123	1.453	5.540	2.967
	Simulated mean	0.347	0.874	7.134	0.474	1.120	6.667	0.121	0.929	3.543	0.123	1.171	3.263	2.224
	Model errors	0.151	0.095	0.048	0.167	0.167	0.191	0.301	0.338	0.328	0.070	0.153	0.222	0.172
NO_2^--N	Observed mean	0.166	0.451	0.751	0.157	0.239	0.456	0.034	0.094	0.392	0.040	0.163	0.307	0.281
	Simulated mean	0.147	0.250	1.925	0.130	0.323	2.016	0.053	0.251	0.248	0.092	0.529	0.893	0.593
	Model errors	0.082	0.527	0.477	0.151	0.164	0.701	0.277	0.597	0.301	0.489	0.580	0.588	0.574
NO_3^--N	Observed mean	1.617	2.791	15.499	1.429	2.006	11.496	1.850	4.670	9.721	3.333	7.175	13.969	6.287
	Simulated mean	1.670	3.558	18.446	1.181	2.810	15.239	1.807	4.458	9.612	3.130	6.517	14.241	6.954
	Model errors	0.035	0.146	0.112	0.117	0.184	0.179	0.094	0.076	0.090	0.097	0.086	0.027	0.119
Total nitrogen	Observed mean	3.560	6.152	31.454	3.804	5.717	24.716	2.910	7.454	17.584	4.810	10.667	23.041	11.966
	Simulated mean	3.580	6.550	33.490	3.600	6.480	29.330	3.060	7.110	16.710	4.700	11.020	23.390	12.619
	Model errors	0.030	0.075	0.049	0.041	0.103	0.112	0.029	0.027	0.023	0.027	0.023	0.030	0.070

as they represent the totality of measurements of any given nitrogen forms. Taking into account the existing analytical error in measurements of nitrogen forms (as ± 15%), it is possible to conclude that mean values of the nitrogen compounds estimated on the basis of modeling are close to those evaluated from experimental data and as a whole, the observations and computed values are representative of a similar population. This may be also confirmed in the analysis of variances by the so-called variance ratio or F-test that is defined as the ratio of larger to the smaller of the two variance estimates for two data sets, s_1^2 and s_2^2:

$$F = s_1^2 / s_2^2 \quad . \tag{6}$$

This test applied for the comparison of two small data sets was used to evaluate how the given model described the fluctuation of individual nitrogen forms in each of the experiments. Calculated values of F are presented in Table 9 and they should be compared with the variance ratio taken from tables of the F-distribution (Bailey, 1959). These values for the 5% level of significance and known degrees of freedom are shown at the top of Table 9. The comparison of F values shows that computed F values as a rule are smaller than values of statistical F distribution and therefore, it is possible to conclude that variances of mean in two groups of data, observations and simulations, are homogeneous so far we can tell from such small data sets. The exclusion may be done for variances of PON in experiments 3 and 9 (i.e., where nitrogen levels were high) and for variance of nitrite-N in experiments 3, 6, 8 and 10-12.

Table 9. Test for Comparison of Variances of Nitrogen Concentrations for Individual Experiments (n=8 for expts. 1-6; n=7 for expts. 7-9, 12; n=6 for expts. 10,11)

Characteristics	Experiments											
	1	2	3	4	5	6	7	8	9	10	11	12
Statistic value of F-distribution	3.79	3.79	3.79	3.79	3.79	3.79	4.28	4.28	4.28	5.05	5.05	4.28
DON	1.65	1.78	1.48	1.29	1.39	1.95	1.14	1.10	3.03	2.21	2.37	1.77
PON	1.70	1.90	4.86	1.19	1.06	1.34	1.60	1.85	5.28	2.45	1.16	1.50
TON	1.06	1.00	1.86	1.30	1.24	1.56	1.09	1.23	1.22	1.06	1.56	1.67
NH_4^+-N	1.19	1.23	1.14	1.14	1.17	1.30	1.32	1.55	1.46	1.18	1.39	1.70
NO_2^--N	1.02	2.41	7.90	1.72	1.93	31.85	3.03	13.89	1.93	8.30	13.94	13.28
NO_3^--N	1.04	1.67	1.48	1.55	2.03	1.73	1.12	1.16	1.14	1.20	1.27	1.05
Total N	1.01	1.11	1.13	1.12	1.25	1.37	1.10	1.10	1.11	1.05	1.07	1.03

However, both of these nitrogen forms are measured with a small accuracy because the analytical difficulty (for PON) and the rapid concentration changes during active nitrification phase (for nitrite-N).

The examination of variances of individual nitrogen fractions for samples generalized for all experiments (where total number of data is great and n=88) to determine whether there is any real differences in mean values between two groups of data may be made by formula

$$d = \frac{x_1 - x_2}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}}, \qquad (7)$$

where x_1, s_1 and n_1 are mean, standard deviation and number of data in first sample and x_2, s_2 and n_2 are the same characteristics for the second sample (Bailey, 1959). Computed values of d are presented in Table 10. According to statistics, if absolute value of d is smaller than 1.96 then we can conclude that there is no significant difference between means in both samples at the 5% level of significance. Our calculated values of d in Table 10 are smaller than 1.96 and they equal to 0.42, 0.44, 0.60, 0.77, 0.86, 1.25 and 1.28 for total N, PON, NO_3^--N, NH_4^+-N, TON, DON and NO_2^--N, respectively.

Using the nitrogen concentrations measured in experiments and simulated in computer runs, the model errors (ρ) in the

Table 10. Tests for Comparison of Variances of Nitrogen Concentrations in Data Sets generalized for all Experiments (n=88)

Nitrogen forms	DON	PON	TON	NH_4^+-N	NO_2^--N	NO_3^--N	Total N
d	1.25	0.44	0.86	0.77	1.28	0.60	0.42

description of the nitrogen transformations may be calculated by Theil's formula (Theil, 1961):

$$\rho = \frac{\sqrt{1/n \; \Sigma (N_i^{obs} - N_i^{sim})^2}}{\sqrt{1/n \; \Sigma (N_i^{obs})^2} + \sqrt{1/n \; \Sigma (N_i^{sim})^2}} \quad , \qquad (8)$$

where N_i^{obs} and N_i^{sim} are observed and simulated nitrogen concentrations respectively, i is number of sample and n is total number of data in each set. ρ is the index that measures the degree to which a simulation model describes the nitrogen observations. This index varies between 0 and 1. If $\rho = 0$, the model description of the nitrogen dynamics observed in experiments is perfect.

Values of the model errors, ρ, computed for individual nitrogen fractions are presented in Table 8. Thus, the average errors in the simulation of the dynamics of individual nitrogen forms are 0.070 (total N); 0.119 (NO_3^--N); 0.172 (NH_4^+-N); 0.221 (TON); 0.234 (DON); 0.330 (PON); and 0.574 (NO_2^--N).

In an attempts to seek a quantitative relationship between the nitrogen concentrations in observed and simulated time series, the method of regression analysis was also used. The simplest

form of the relationship may be presented by linear regression equation

$$Y = a + b \cdot X \quad , \tag{9}$$

where Y and X are the observed and simulated nitrogen concentrations, respectively; a and b are regression coefficients, intercept and slope, respectively.

Standard linear regression statistics were computed by applying equation (9). This includes (i) calculations of the regression coefficient values, a and b; (ii) t-statistics, i.e., tests of significance for the slope coefficient, b, (which is generally of most interest), with the null hypothesis on the slope and 5% level of probability; (iii) the square of the correlation coefficient, r^2, between observed and computed concentrations of nitrogen fractions.

These statistical criteria are considered to be sufficient for providing a comprehensive evaluation of the agreement between simulation results and observations. The results of computations of standard linear regression statistics are shown in Table 11 (for the nitrogen fractions) and in Table 10 (for the individual experiments).

The statistics in Table 11 shows that a good correlation is obtained with a regression line slope close to 1 (i.e., b=1, excluding b=0.615 for DON and b=0.249 for nitrite-N) but for the intercept, $a \neq 0$, which may be explained by the existing accuracy of the analytical nitrogen measurements (see Tables 1-4). However, a highly significant values of t-ratio* in

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*t-ratio is equal to $\hat{b}$ divided on standard error in b evaluation.

Table 11. Standard Linear Regression Statistics for Relationship between Observed and Computed Nitrogen Concentrations (obtained for all Time Series, n=88)

Regression coefficients	Nitrogen fractions						
	DON	PON	TON	NH_4^+-N	NO_2^--N	NO_3^--N	Total-N
a	0.334	-0.224	-0.277	0.672	0.134	0.553	0.532
b	0.615 (9.8)	1.098 (8.0)	1.000 (11.8)	1.032 (26.0)	0.249 (13.5)	0.824 (33.8)	0.906 (47.2)
r^2	0.527	0.427	0.619	0.887	0.678	0.930	0.963

Table 11 given in brackets below the values of coefficients, b, for the different nitrogen fractions, show that the linear relationship between data in two sets is rather representative and values of b are highly realistic. In other words, the hypothesis that b=0 would be rejected at 5% level of significance because for all nitrogen fractions, t-ratios are much larger than 1.99 for n=88. This value can be found from table of the t-distribution with n=2 degrees of freedom (Allard, 1977). The similar conclusion is even more apparent when we begin the analysis of statistics in Table 12. It shows that in the different experiments the relationship between nitrogen concentrations in observed and simulated time series is linear with a slope ranging between 0.873-1.053 and with a t-ratio varying between 18.8 and 37.0. The values of a regression coefficients, a and b, averaged for the twelve experiments, are equal to 0.163 and 0.908, respectively, and this total relationship is very significant (t-ratio is 91.7). Therefore, we can again reject the hypothesis that b=0 because in all cases, t-ratios are much more significant than 2.423 obtained for minimal n=42 from the table of the t-distribution with n=2 degrees of freedom (Allard, 1977).

Finally, the values of r^2, estimated in this analysis and also presented in Tables 11 and 12, may be used as an additional s criterion in the evaluation of the model adequacy. The values of r^2 may vary from 0 to 1 and if r^2 equal to 1 then the correlation between two quantities is perfect. For the given nitrogen fractions the r^2 statistics lies in the range 0.43-0.96 while for samples generalized for individual experiments r^2 is in the range 0.87 to 0.96. The mean value of r^2 for all the data is estimated to be equal to 0.932.

Table 12. Standard Linear Regression Statistics for Relationship between all observed and computed Nitrogen Concentrations (obtained for individual Experiments)

No. of Experiments	Regression Coefficients		
	a	b	r^2
1	-0.008	0.997 (37.0)	0.962
2	0.158	0.873 (24.7)	0.919
3	0.788	0.896 (32.7)	0.952
4	-0.019	1.037 (33.4)	0.954
5	0.109	0.835 (22.4)	0.903
6	0.148	0.819 (18.8)	0.867
7	-0.056	0.991 (28.8)	0.946
8	-0.036	1.048 (28.1)	0.944
9	0.213	1.020 (20.5)	0.900
10	-0.054	1.053 (28.6)	0.953
11	-0.379	1.039 (27.8)	0.951
12	-0.210	0.990 (31.9)	0.956
Average	0.163	0.908 (91.7)	0.932

Discussion

Many of the important characteristics of nitrogen transformation processes that cannot be obtained directly from the measurements of chemical and biological compound concentrations may be comparatively easily estimated by an analysis of simulation results. We shall, therefore present some examples of the analysis of these results in order to obtain additional insights, into nitrogen transformation processes under the controlled experiments with water from Slnava Reservoir.

The first example concerns estimation of the bacterial activity in the conversion of nitrogenous matter. Usually this information can only be obtained from specialized and time-consuming experimental studies (Srinath et al., 1976) in evaluating the role of individual bacteria (heterotrophs as well as nitrifiers) in the oxidation of different nitrogen sources. The actual activity of bacteria in transforming the nitrogen compounds from one form to another at any time is dependent upon: (i) the biomass concentration of active bacterial forms; (ii) the concentration of substrate for bacterial growth, and (iii) temperature, according to the hypotheses used for the construction of our model. The possible effect of other environmental factors, such as oxygen and pH, were considered to be negligible for the conditions of the experiments analyzed in this study.

Because the natural bacterial population are heterogenous assemblages of microorganisms with widely different physiological characteristics (such as size, generation time, nutritional requirements), the direct application of a simple mathematical

model in the description of bacterial activities has been questioned (Williams, 1973). However, in the literature there are many examples of evaluations of relative microbial activities in different water bodies as well as within the same water (Sibert and Brown, 1975; Hobbie et al., 1972).

Using the simulation results of this study, the bacterial activities in nitrogen transformation may be evaluated in at least two ways. The first one is based on consideration of bacterial excretion activities. As noted previously, the introduction of microorganism activity into an ecological model describing the nitrogen cycle, allows a detailed simulation of the dynamics of nitrogen fractions obtained in experiments with sewage, river, lake and sea water samples (Leonov, 1980).

Substrate utilization by growing bacteria and the growth of biomass are not equivalent processes because not all of the substrate taken up by bacteria is included in the cell composition. Only a small part of substrate utilized is absorbed into the biomass while the major part of the metabolized substrate is excreted as a waste product. Table 13 summarizes the evaluation of excretion activities by heterotrophs and nitrifiers as obtained from the given model. As can be seen from Table 13, the variation in the excretion activity of each type of bacteria during their growth phase is similar in the different experiments and primarily it depends on the initial concentration of substrate taken up in bacterial growth.

In the concentration range of dissolved organic-N, given by experimental conditions, the excretion activity of heterotrophs varies slightly between 0.61-0.65 of the rate of substrate uptake. It is important to observe that in the given

Table 13. Excretion Activities of Bacteria as calculated by Model

Experiment numbers	Bacteria	Growth phases of bacteria									
		Lag		Logarithmic			Mortality		Steady-state		
		period, days	r_{Bi}	period, days	r_{Bi}	biomass peak, mgN/ℓ	period, days	r_{Bi}	period, days	r_{Bi}	biomass mgN/ℓ
1	Heterotrophs	-	-	0-4	0.62-0.64	0.083	4-10	0.61-0.62	10-60	0.61	0.040
	Nitrosomonas	0-2	0.86	4-10	0.34-0.86	0.337	10-60	0.35-0.39	-	-	-
	Nitrobacter	0-4	0.77-0.88	4-36	0.49-0.97	0.088	36-60	0.48-0.49	-	-	-
2	Heterotrophs	-	-	0-4	0.62-0.64	0.083	4-10	0.61-0.62	-	-	-
	- " - " -	-	-	10-16	0.62	0.062	16-60	0.62	-	-	-
	Nitrosomonas	0-2	0.87	4-10	0.32-0.86	0.563	12-60	0.34-0.39	-	-	-
	Nitrobacter	0-4	0.88-0.96	4-36	0.49-0.98	0.123	36-60	0.48-0.49	-	-	-
3	Heterotrophs	-	-	0-4	0.62-0.64	0.102	5-8	0.62	-	-	-
	- " - " -	-	-	8-32	0.61-0.62	0.181	32-60	0.60	-	-	-
	Nitrosomonas	0-2	0.89	4-12	0.29-0.89	2.500	12-30	0.29-0.38	30-60	0.39	0.900
	Nitrobacter	0-6	0.95-0.97	6-18	0.50-0.97	0.406	18-24	0.47-0.49	26-60	0.49	0.390
4	Heterotrophs	-	-	0-5	0.61-0.65	0.035	5-12	0.62	-	-	-
	- " - " -	-	-	12-30	0.62	0.024	30-60	0.62	-	-	-
	Nitrosomonas	0-2	0.80	4-12	0.30-0.80	0.340	12-30	0.30-0.38	30-60	0.39	0.117
	Nitrobacter	0-4	0.70-0.89	6-18	0.42-0.96	0.071	18-30	0.42-0.48	30-60	0.48	0.050
5	Heterotrophs	-	-	0-5	0.61-0.65	0.033	5-12	0.62	-	-	-
	- " - " -	-	-	12-34	0.62	0.031	34-60	0.62	-	-	-
	Nitrosomonas	0-4	0.83	4-11	0.30-0.82	0.700	11-26	0.27-0.37	26-60	0.39	0.150
	Nitrobacter	0-4	0.84-0.87	4-17	0.45-0.97	0.120	17-40	0.38-0.48	40-60	0.48	0.066
6	Heterotrophs	-	-	0-5	0.62-0.65	0.034	5-12	0.62	-	-	-
	- " - " -	-	-	12-42	0.62	0.075	44-60	0.62	-	-	-
	Nitrosomonas	0-2	0.84	4-13	0.30-0.84	2.900	13-42	0.26-0.39	44-60	0.39	0.380
	Nitrobacter	0-6	0.94	6-18	0.65-0.97	0.580	18-44	0.33-0.48	46-60	0.48	0.160
7	Heterotrophs	-	-	0-4	0.62-0.64	0.117	4-16	0.62	16-40	0.62	0.035
	Nitrosomonas	0-2	0.76	2-10	0.39-0.81	0.248	10-40	0.37-0.39	-	-	-
	Nitrobacter	0-4	0.76-0.91	4-28	0.48-0.96	0.077	28-40	0.48	-	-	-
8	Heterotrophs	-	-	0-4	0.62-0.64	0.117	4-40	0.62	-	-	-
	Nitrosomonas	0-2	0.87	2-8	0.35-0.87	0.498	8-40	0.35-0.38	-	-	-
	Nitrobacter	0-4	0.93-0.96	4-30	0.50-0.97	0.135	30-40	0.49	-	-	-
9	Heterotrophs	-	-	0-4	0.62-0.64	0.113	4-8	0.62	-	-	-
	- " - " -	-	-	8-18	0.62	0.146	18-40	0.42	-	-	-
	Nitrosomonas	0-2	0.88	2-9	0.33-0.88	1.300	9-40	0.33-0.38	-	-	-
	Nitrobacter	0-4	0.96-0.97	4-34	0.49-0.97	0.284	34-40	0.49	-	-	-
10	Heterotrophs	-	-	0-3	0.63	0.150	3-50	0.62	-	-	-
	Nitrosomonas	0-2	0.79	2-12	0.40-0.82	0.305	12-50	0.38-0.39	-	-	-
	Nitrobacter	0-4	0.83-0.92	4-30	0.49-0.96	0.102	30-50	0.48-0.49	-	-	-
11	Heterotrophs	-	-	0-3	0.62-0.63	0.252	3-50	0.62	-	-	-
	Nitrosomonas	0-2	0.88	2-9	0.38-0.87	0.780	9-50	0.38-0.39	-	-	-
	Nitrobacter	0-4	0.93-0.96	4-34	0.49-0.98	0.234	34-50	0.48-0.49	-	-	-
12	Heterotrophs	-	-	0-3	0.62-0.63	0.350	3-10	0.62	10-50	0.62	0.200
	Nitrosomonas	0-2	0.88	2-10	0.35-0.88	0.563	10-30	0.35-0.38	30-50	0.38	1.000
	Nitrobacter	0-4	0.96-0.97	4-36	0.49-0.97	0.424	36-50	0.48-0.49	-	-	-

experiments the excretion activity of heterotrophs was practically constant during their different growth phases.

The excretion activity of nitrifiers is significantly different in the various experiments as a result of widely different initial concentrations of the substrates, ammonium-N and nitrite-N, taken up by Nitrosomonas and Nitrobacter, respectively. According to simulation results in the development of nitrifiers, it is possible to recognize the lag, logarithmic, mortality and sometimes a steady state growth phases. The excretion activity of nitrifiers is largest in the lag phase when, in the different experiments, it is equal to 0.76-0.89 for Nitrosomonas and 0.83-0.97 for Nitrobacter. This means that 11-24% and 3-17% of the substrate utilized by Nitrosomonas and Nitrobacter, respectively, spent on the construction of biomass and the remainder is excreted in a transformed form to the water environment.

In the logarithmic growth phase the excretion activity of nitrifiers varies over a large range: from 0.3 to 0.88 for Nitrosomonas and from 0.29 to 0.98 for Nitrobacter. During the mortality growth phase the excretion is equal to 0.29-0.39 and 0.33-0.49 of the uptake rate for Nitrosomonas and Nitrobacter, respectively, and in the steady state growth phase it is about 0.38-0.39 and 0.48-0.49 for the same bacteria. Thus, in the final growth phases the excretion activities of the bacteria fluctuate over a small range depending on the substrate concentration.

The oxidative potential of bacteria, which is often used as an indicator of the quality of a water environment (Zubkoff and Wariner, 1977), is a second criterion for assessing bacterial

activity that may be evaluated from the simulation results. This characteristic is calculated as a product of the specific rate of substrate uptake and the bacterial biomass at any given time. Thus it is possible to estimate the direct quantitative effect, or functional efficiency, of bacteria in transforming the nitrogenous matter for different initial concentrations of the nitrogen sources and in various growth phases of the bacteria. The oxidative potential of the bacteria is most useful for understanding the role of the different bacterial groups in water polluted by nitrogen sources. Evaluation of the oxidative potential of the heterotrophs and nitrifiers is presented in Table 14 for the different experiments. Actually these estimates show the rates of substrate uptake by different bacteria and they are a result of the environmental conditions (temperature, nutrient contents and bacterial activities).

The lag phase of bacterial growth, accounted for in the modeling results only for nitrifiers, is characterized by the lowest values of oxidative potential in comparison with the other growth phases. In all experiments the values of oxidative potential of the nitrifiers vary from 0.01 to 0.13 mg N/ℓ-day (for Nitrosomonas) and from 0.002 to 0.152 mg N/ℓ-day (for Nitrobacter); during the lag growth phase the temperature has a slight influence on the efficiency of nitrifiers in transforming the mineral nitrogen sources. It is also important that the oxidative potential of nitrifiers during the lag growth phase is not dependent on the initial substrate concentrations.

In a logarithmic growth phase the oxidative potential of the bacteria varies over a large range and its highest values

Table 14. Oxidative Potential of Bacteria in mg N/ℓ-day as calculated by Model

Experiment numbers	Bacteria	Growth phases of bacteria							
		Lag		Logarithmic		Mortality		Steady-state	
		period days	oxidative potential	period days	oxidative potential	period days	oxidative potential	period days	oxidative potential
1	Heterotrophs	-	-	0-4	0.206-0.312	4-10	0.112-0.135	10-60	0.095-0.124
	Nitrosomonas	0-2	0.018	4-10	0.070-0.915	10-60	0.057-0.077	60	0.057*
	Nitrobacter	0-4	0.002-0.007	4-36	0.025-0.438	36-60	0.022-0.025	60	0.022*
2	Heterotrophs	-	-	0-4	0.208-0.313	4-10	0.122-0.140	-	-
	- " - " -	-	-	10-16	0.132-0.172	16-60	0.139-0.169	60	0.139*
	Nitrosomonas	0-2	0.022	4-10	0.077-1.591	10-60	0.077-0.102	60	0.084*
	Nitrobacter	0-4	0.005-0.014	4-36	0.036-0.811	36-60	0.032-0.036	60	0.032*
3	Heterotrophs	-	-	0-4	0.211-0.248	5-8	0.162-0.165	-	-
	- " - " -	-	-	8-32	0.165-0.497	32-60	0.484-0.495	60	0.484*
	Nitrosomonas	0-2	0.026	4-12	0.115-9.880	12-30	0.193-0.300	30-60	0.294-0.300
	Nitrobacter	0-6	0.016-0.035	6-18	0.093-5.003	18-24	0.102-0.600	26-60	0.112-0.114
4	Heterotrophs	-	-	0-5	0.035-0.105	5-12	0.048-0.074	-	-
	- " - " -	-	-	12-30	0.049-0.066	30-60	0.059-0.065	60	0.059*
	Nitrosomonas	0-2	0.010	4-12	0.034-0.658	12-30	0.030-0.037	30-60	0.036-0.039
	Nitrobacter	0-4	0.001-0.003	6-18	0.010-0.326	18-30	0.013-0.014	30-60	0.014-0.015
5	Heterotrophs	-	-	0-5	0.035-0.105	5-12	0.048-0.075	-	-
	- " - " -	-	-	12-34	0.061-0.086	34-60	0.079-0.085	60	0.079*
	Nitrosomonas	0-4	0.039-0.047	4-11	0.173-1.874	11-26	0.029-0.050	30-60	0.047-0.051
	Nitrobacter	0-4	0.003-0.007	4-17	0.022-0.778	17-40	0.014-0.022	40-60	0.018-0.020
6	Heterotrophs	-	-	0-5	0.033-0.100	5-12	0.051-0.075	-	-
	- " - " -	-	-	12-42	0.077-0.207	44-60	0.200-0.207	60	0.200*
	Nitrosomonas	0-2	0.015-0.057	4-13	0.057-12.010	13-42	0.046-0.124	44-60	0.120-0.124
	Nitrobacter	0-6	0.011-0.048	6-19	0.127-5.300	19-44	0.027-0.048	46-60	0.046-0.048
7	Heterotrophs	-	-	0-4	0.284-0.457	4-16	0.118-0.185	16-40	0.088-0.114
	Nitrosomonas	0-2	0.032	2-10	0.083-0.396	10-40	0.053-0.129	40	0.053*
	Nitrobacter	0-4	0.004-0.023	4-28	0.023-0.221	28-40	0.020-0.023	40	0.020*
8	Heterotrophs	-	-	0-4	0.288-0.453	4-40	0.161-0.201	40	0.161*
	Nitrosomonas	0-2	0.104	2-8	0.112-1.581	8-40	0.096-0.121	40	0.096*
	Nitrobacter	0-4	0.027-0.090	4-30	0.040-0.893	30-40	0.037-0.040	40	0.037*
9	Heterotrophs	-	-	0-4	0.297-0.362	4-8	0.228-0.240	-	-
	- " - " -	-	-	8-18	0.240-0.401	18-40	0.347-0.400	40	0.347*
	Nitrosomonas	0-2	0.125	3-9	0.549-3.720	9-40	0.191-0.241	40	0.209*
	Nitrobacter	0-4	0.055-0.131	4-34	0.083-2.917	34-40	0.080-0.083	40	0.080*
10	Heterotrophs	-	-	0-3	0.319-0.476	3-50	0.113-0.235	50	0.113*
	Nitrosomonas	0-2	0.040	2-12	0.102-0.486	12-50	0.068-0.097	50	0.068*
	Nitrobacter	0-4	0.008-0.036	4-30	0.030-0.298	30-50	0.026-0.030	50	0.026*
11	Heterotrophs	-	-	0-3	0.564-0.761	3-50	0.265-0.446	50	0.265*
	Nitrosomonas	0-2	0.117	2-9	0.239-2.061	9-50	0.159-0.230	50	0.159*
	Nitrobacter	0-4	0.031-0.104	4-34	0.068-1.385	34-50	0.061-0.067	50	0.061*
12	Heterotrophs	-	-	0-3	0.745-0.866	3-20	0.575-0.617	20-50	0.500-0.600
	Nitrosomonas	0-2	0.130	2-10	0.345-9.260	10-30	0.338-0.368	30-50	0.391-0.333
	Nitrobacter	0-4	0.067-0.152	4-36	0.125-3.459	36-50	0.116-0.125	50	0.116*

are obtained in the early stages of logarithmic growth when the bacteria biomass is low and the amount of substrate for a particular biomass unit is sufficient to maintain active growth of the bacterial groups. As a whole a maximum value of the oxidative potential of heterotrophs as well as nitrifiers is primarily dependent on the initial substrate concentration used by bacteria for growth. It is also defined by the rates of substrate formation for the external nutrient cycling by chemical-biological transformation of the nitrogen sources.

The highest values of the oxidative potential for Nitrosomonas (9.8-12.0 mg N/ℓ-day) were estimated for the 18° C experiments 3,6 and 12), where a high initial concentration of ammonium-N (30.3, 25.7 and 14.8 mg N/ℓ, respectively) was available. At an initial ammonium-N concentration of 0.3-4.7 mg N/ℓ (in experiments 1, 2, 7, 8, 10 and 11) the values of Nitrosomonas oxidative potential were significantly lower and equal to 0.4-2.1 mg N/ℓ-day. The maximum oxidative activity of Nitrobacter was estimated to be equal to 2.9-5.0 mg N/ℓ-day in the 18° C experiments (3, 9 and 12) with initial nitrite-N contents of 0.34-0.72 mg N/ℓ. For the 12° C experiments the oxidative potential of nitrifiers varied in the same manner as for the 18° C tests.

The oxidative potential of the heterotrophs during the logarithmic growth phase varies over the range of 0.21-0.31 mg N/ℓ-day for the 18°C experiments (1-3) with initial DON contents of 0.71 mg N/ℓ. Increasing the initial DON concentrations in experiments (7-9) to 0.86 mg N/ℓ and in experiments (10-12) to 1.26-2.24 mg N/ℓ brings about a corresponding increase of the oxidative potential of heterotrophs so that the range of its

fluctuations was 0.28-0.46 mg N/ℓ-day (in experiments 7-9) and 0.32-0.87 mg N/ℓ-day (in experiments 10-12). For the 12° C experiments the values of the oxidative potential of heterotrophs during the logarithmic growth phase is about 3 times lower than in the 18° C tests.

In the mortality phase the oxidative potential of bacteria is about 3-10 times lower than in the logarithmic growth phase. Its values vary over a relatively narrow range depending upon the production of the substrate by internal transformation processes of nitrogen sources.

In a steady-state phase the values of the oxidative potential of bacteria, heterotrophs as well as nitrifiers, are pratically constant and they reflect an equilibrium state in the rates of the individual stages of the chemical-biological transformations of the nitrogen compounds. The values of the oxidative potential in a steady-state growth phase show also new equilibrium levels in the bacterial activities attained after the transient oxidative processes of nitrogen conversion are completed.

The values of the oxidative potential of bacteria estimated from the simulation results for different experimental tests may be considered as quite reliable since the model is able to reproduce the concentration changes in the nitrogen fractions as observed in the experiments. As for the biomasses of bacteria and the specific rates of substrate uptake by bacteria, these values may be reproduced by model to a certain degree of accuracy only when experimental data on the dynamics of biomass population changes are available.

One of the important problems of water quality studies is evaluation of the influence of nitrogen transformation processes on the oxygen balance. The model considered in this report gives an opportunity to assess the dynamics of oxygen as a result of nitrogen conversion. This information is important for a quantitative understanding of the self-purification capacity of water bodies that are polluted by nitrogen sources. In the literature there are many examples of the application of different models to describe the oxygen dynamics resulting from nitrogen transformations in natural waters and wastewater treatment plants (Downing and Knowles, 1971; Tuffey et al., 1974; Anderson et al., 1976; Lopez-Bernal et al., 1977; Miller and Jennings, 1979).

Figure 15 shows the hypothetical curves for the oxygen dynamics in the experiments according to the different nitrogen concentrations transformed by bacteria. The decrease of the oxygen levels in these experiments must be caused by bacterial oxygen consumption during the oxidation of organic and mineral nitrogen sources, while the increase depends only on reaeration, which in all cases was considered to be similar. In the simulation runs the rate constant of reaeration was taken to be equal to 1.25 day^{-1} (Sornberger and Keshavan, 1973) taking into account that at laboratory conditions the continuous aeration brought by stirring. The modeling results show that for high initial concentrations of the nitrogen fractions (primarily the ammonium-N) this constant rate of reaeration is not sufficient to maintain the aerobic conditions during all the experiment. This rate must therefore be higher and equal at least to 3 day^{-1} (Leonov, 1980).

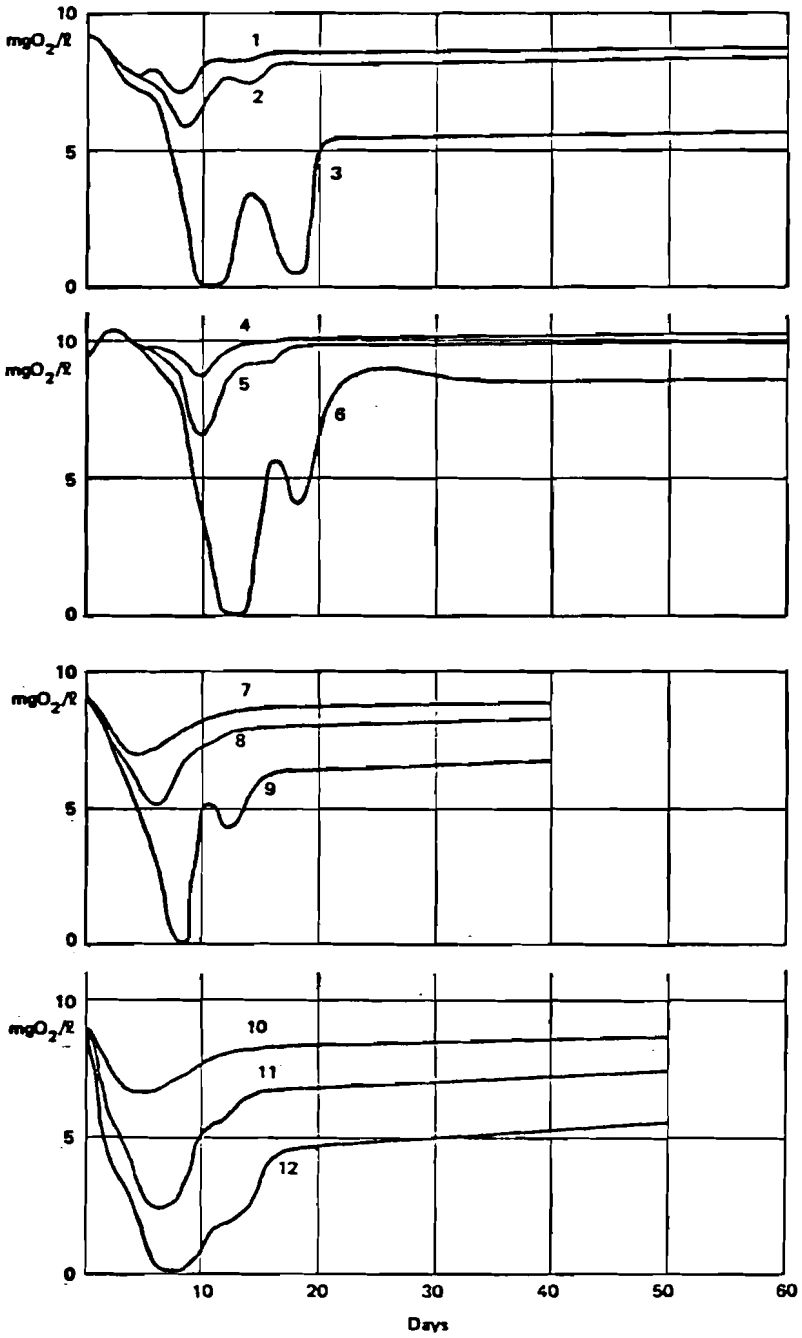

Figure 15. Predicted Effects of Nitrogen Transformation on the Dissolved Oxygen Dynamics in Experiments 1-12

After the oxidative nitrogen transformation is completed the oxygen contents in experiments increased mainly by reaeration. In the water samples with the lowest initial nitrogen concentrations these oxygen concentrations will be close to saturation. Principally the level of oxygen in the final steps of the experiments shows the balance between all the oxidative processes of the nitrogen sources during the whole period studied. In experiments with a high initial concentration of nitrogen forms the final oxygen level is less than the saturation oxygen content by 3.7 mg O_2/ℓ (experiments 3 and 12) and 2.5 mg O_2/ℓ (experiment 9).

Using the model it is also possible to estimate the oxygen consumption by the different types of bacteria. The data presented in Table 15 shows the dynamics of bacterial oxygen consumption during the oxidation of the nitrogen fractions, which is dependent on bacterial activities. The highest values of bacterial oxygen consumption take place during the logarithmic growth phase, after which the intensity of oxygen consumption by bacteria is significantly decreased. However the values of oxygen consumption show that the bacteria continue to metabolize the nitrogen sources after the active stages of nitrogen transformations are completed. After approximately twenty days of water incubation this is difficult to establish from the data on the nitrogen compound concentrations because they are dependent on the equilibrium between the main processes of nitrogen conversion in the water, such as bacterial nitrogen utilization, excretion of transformed nitrogen forms and the decomposition of non-living particulate nitrogen to dissolved organic-N.

Table 15. Cumulative Values of Bacterial Oxygen Consumption (mg O_2/ℓ) as calculated by Model

Experiment numbers	Bacteria	Time in days								
		4	8	12	16	20	30	40	50	60
1	Heterotrophs	5.83	10.56	14.36	18.62	22.80	32.66	41.84	50.42	58.48
	Nitrosomonas	0.28	4.41	6.87	7.26	7.64	8.57	9.44	10.26	11.02
	Nitrobacter	0.01	0.20	1.38	2.27	2.34	2.50	2.64	2.77	2.89
2	Heterotrophs	5.85	10.76	15.22	20.78	26.41	40.05	53.00	65.32	77.08
	Nitrosomonas	0.36	6.65	14.04	14.52	15.04	16.33	17.56	18.74	19.86
	Nitrobacter	0.02	0.34	2.32	4.65	4.74	4.96	5.16	5.35	5.53
3	Heterotrophs	5.55	11.17	18.55	32.11	47.74	88.38	129.26	169.80	209.95
	Nitrosomonas	0.44	9.18	88.08	89.15	90.49	94.28	98.22	102.15	106.05
	Nitrobacter	0.08	0.57	3.46	15.55	29.08	29.70	30.34	30.98	31.62
4	Heterotrophs	1.51	4.03	5.65	7.48	9.59	15.00	20.38	25.58	30.57
	Nitrosomonas	0.13	1.68	5.34	5.47	5.64	6.13	6.64	7.14	7.61
	Nitrobacter	0.01	0.06	0.55	1.68	1.74	1.82	1.90	1.98	2.06
5	Heterotrophs	1.51	4.04	5.69	7.72	10.28	17.16	24.21	31.10	37.74
	Nitrosomonas	0.18	2.64	12.71	12.85	13.05	13.65	14.32	14.98	15.62
	Nitrobacter	0.01	0.14	1.10	4.06	4.18	4.27	4.37	4.48	4.58
6	Heterotrophs	1.46	3.97	5.73	8.38	13.07	28.10	44.92	61.97	78.72
	Nitrosomonas	0.23	3.63	53.16	73.59	73.92	75.15	76.72	78.36	79.97
	Nitrobacter	0.05	0.29	1.83	8.47	24.13	24.29	24.53	24.79	25.05
7	Heterotrophs	8.36	14.82	19.36	23.42	27.18	35.73	43.38	-	-
	Nitrosomonas	0.49	3.21	3.68	4.06	4.41	5.21	5.94	-	-
	Nitrobacter	0.03	0.50	1.13	1.21	1.27	1.40	1.52	-	-
8	Heterotrophs	8.32	15.38	21.93	28.59	35.01	49.99	63.77	-	-
	Nitrosomonas	1.66	11.43	12.02	12.64	13.24	14.66	15.97	-	-
	Nitrobacter	0.15	1.49	3.96	4.07	4.18	4.41	4.63	-	-
9	Heterotrophs	7.97	15.92	26.34	39.28	52.49	84.10	113.60	-	-
	Nitrosomonas	2.12	37.10	38.64	39.82	41.06	44.07	46.89	-	-
	Nitrobacter	0.27	1.96	9.37	13.22	13.43	13.93	14.40	-	-
10	Heterotrophs	9.84	17.86	23.86	29.20	34.16	45.57	55.98	65.63	-
	Nitrosomonas	0.61	3.88	4.51	5.02	5.49	6.57	7.56	8.47	-
	Nitrobacter	0.04	0.72	1.40	1.51	1.59	1.77	1.93	2.08	-
11	Heterotrophs	16.85	31.96	44.63	56.68	68.12	94.64	118.95	141.55	-
	Nitrosomonas	1.89	19.13	20.33	21.47	22.55	25.07	27.38	29.54	-
	Nitrobacter	0.17	1.75	6.64	6.87	7.07	7.50	7.87	8.22	-
12	Heterotrophs	21.92	42.63	61.65	81.77	101.82	149.70	194.50	236.81	-
	Nitrosomonas	2.21	43.10	52.26	54.11	56.00	60.55	64.84	68.90	-
	Nitrobacter	0.33	2.23	10.70	17.96	18.30	19.08	19.78	20.44	-

In analyzing the simulation results on the oxygen dynamics it is clear that further experimental studies are needed to quantify accurately the effects of nitrogen transformations on the oxygen balance.

Conclusions

The main purpose of this study was to examine further the nitrogen transformation model developed previously by Leonov (1980). Because this model describes well the individual biochemical processes in nitrogen transformation by non-linear kinetics, it was assumed that its simulation ability in the prediction of nitrogen compound dynamics is higher than the "simpler" first-order models and that it may therefore reproduce the features of nitrogen conversion in a wide variety of environmental conditions. The first experience in applying this model has allowed us to identify the set of rate coefficients describing nitrogen transformation in quite different water, such as sewage (with a highly active bacterial community), river water (with a high level of ammonium-nitrogen as a result of the river pollution by domestic and industrial waste products) and lake and sea waters (with a natural level in the concentrations of nitrogen forms).

For the next step of model application for the prediction of future events in field conditions or the expected variations of nitrogen levels and water quality in general, it is desirable to test the model's simulation capabilities for possible responses of a system to changeable levels of nutrients and temperature.*

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*These characteristics are considered to be principal ones in regulating the rates of chemical-biological transformation of substances in natural waters.

In this case the comparison of modeling results with field observations may give a reasonable basis for understanding how well the model describes a real set of observations and to find thus the limitation of the model.

The results of this study show that the given model can predict the behavior of nitrogen compounds for a wide variety of initial nitrogen concentrations: 0.71-2.24 mg N/ℓ (for DON); 0.3-30.3 mg N/ℓ (for ammonium-N); 0.014-0.55 mg N/ℓ (for nitrite-N); 0.049-2.53 mg N/ℓ (for nitrate-N). These levels of different nitrogen forms may occur in natural waters of different origin and particularly in the Slnava Reservoir. The accuracy in the model simulation of the dynamics of individual nitrogen fractions according to Theil's criterion is evaluated to be equal to 0.07 (for total N), 0.119 (for nitrate-N), 0.172 (for ammonium-N), 0.221 (for total organic-N), 0.234 (for dissolved organic-N), 0.330 (for particulate organic-N) and 0.574 (for nitrite-N).

It is possible to note that the given model satisfies at least two criteria of model adequacy. Firstly, it gives an acceptable agreement with the nitrogen concentrations observed in experiments and secondly it shows the independence of the rate coefficients from the initial concentrations of the nitrogen forms. The results also suggest the estimated temperature functions for the individual rate constants may be considered as reasonable for the range of temperatures between 12^{o} and 18^{o} C.

Some additional information on the bacterial activity in nitrogen conversion and on the influence of nitrogen oxidation on the oxygen dynamics, obtained from the analysis of simulation

results, shows that the model may give a comprehensive explanation of the observed fluctuations in the various nitrogen forms and may yield quantitative estimates of the rates of individual processes in the nitrogen cycle. Direct assessment of these rates in the field is a very difficult task, because all the processes are in balance and concentrations of all compounds tend to be at a state of dynamical equilibrium.

As a whole the results of this study show that the nitrogen transformation model, examined over a wide set of experimental conditions, may be used for an ecological analysis of the chemical-biological processes occurring in the Slnava Reservoir. For this purpose, this model should now be extended to take into account the basic features of this body such as its hydrodynamics and its morphology.

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