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## AEROBIC NITROGEN TRANSFORMATION IN WATER ENVIRONMENT: EXPERIMENTS AND THEIR MATHEMATICAL SIMULATION

This paper gives experimental data on aerobic nitrogen transformation in water withdrawn from the Slháva Reservoir on the Váh river (Czechoslovakia). The nitrification process was studied in nine experiments covering a broad set of initial concentrations of individual nitrogen forms. These experimental results were analysed with the help of the mathematical model describing the bacterial conversion of nitrogen compounds in water environment. The correlation of experimental and simulated data is evaluated on a statistical basis. Quantitative information on bacterial activity in the process of nitrogen transformation was obtained.

### NOTATIONS

- $b$ ,  $t$ ,  $r^2$  — standard linear regression statistics: slope,  $t$ -ratio and correlation coefficient, respectively,  
 $K_M$  — Michaelis constant, mg N/dm<sup>3</sup>,  
 $Y$  — yield coefficient (unitless),  
 $\mu$  — specific rate of bacterial growth or substrate uptake, day<sup>-1</sup>,  
DON — concentration of dissolved organic nitrogen, mg/dm<sup>3</sup>,  
NH<sub>4</sub><sup>+</sup>-N — concentration of ammonium nitrogen, mg/dm<sup>3</sup>,  
NO<sub>2</sub><sup>-</sup>-N — concentration of nitrite nitrogen, mg/dm<sup>3</sup>,  
NO<sub>3</sub><sup>-</sup>-N — concentration of nitrate nitrogen, mg/dm<sup>3</sup>,  
PON — concentration of particulate organic nitrogen, mg/dm<sup>3</sup>,  
TON — concentration of total organic nitrogen, mg/dm<sup>3</sup>,  
TN — concentration of total nitrogen, mg/dm<sup>3</sup>.

### 1. INTRODUCTION

Nitrogen transformation in water 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

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involving the transformations of nitrogen compounds, the microbiological decomposition of nitrogenous matter takes priority when studying questions of water quality, particularly the self-purification capacity of the water environment. The objective of this paper is to estimate experimentally the intensity of microbiological transformations of nitrogen compounds in water samples from the Sĺňava Reservoir, an important water source built on the Váh river in Slovakia, and to analyse the experimental data by a mathematical model describing the nitrogen oxidation process.

## 2. MODEL EXPERIMENTS

### 2.1. WATER SAMPLING AREA AND EXPERIMENTAL METHODS

The water samples used in experiments were taken from the Sĺňava Reservoir on the Váh river near the town Piešťany. 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  $12.3 \times 10^6 \text{ m}^3$  and the watershed area above the reservoir is  $10.1 \times 10^3 \text{ km}^2$ .

The sampling programme took place in October 1979 and February and April 1980. The water was taken from depths of 0-3 m near the shore of the reservoir, as indicated in fig. 1. Sampling was carried out with a Friedinger sampler and the samples were subsequently transferred to a laboratory. Twenty liter aliquots of the water were distributed

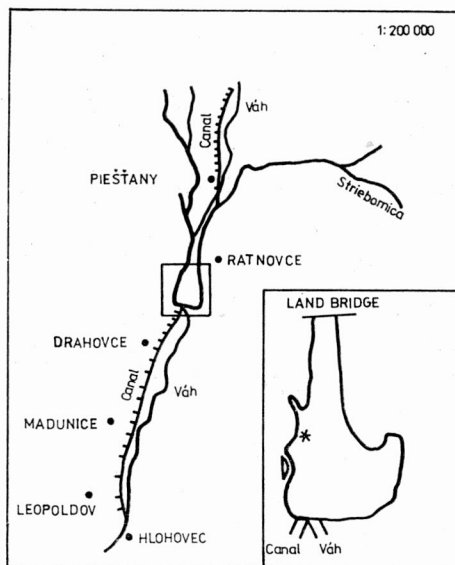


Fig. 1. Map of the Sĺňava Reservoir vicinity with the sampling point indication (\*)  
Rys. 1. Mapa okolic zbiornika Sĺňava ze wskazaniem punktu poboru próbki wody (\*)

into aquaria equipped with aerators. The aquaria were placed in dark conditions at 18°C. Ammonium, nitrite and nitrate were added to two aquaria in the same proportions as determined in the original water sample. The third aquarium was maintained without addition of nitrogen compounds and served as the control unit. At about weekly intervals aliquots of water were taken from the aquaria for chemical analysis as described below.

At the same time experiments were performed at 12°C, but the results are not included in this paper because of space limitations. The complete information on these data is given in the IIASA report by LEONOV and TÓTH [10].

## 2.2. ANALYTICAL METHODS

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 described in this chapter.

### 2.2.1. AMMONIUM-NITROGEN ( $\text{NH}_4^+$ -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  $\text{K}_2\text{HgJ}_4$  in alkaline solution, which produced a brownish-yellow compound.

### 2.2.2. NITRITE-NITROGEN ( $\text{NO}_2^-$ -N)

The photometric method of BENDSCHNEIDER and ROBINSON [4] 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 coloured azocompound.

### 2.2.3. NITRATE-NITROGEN ( $\text{NO}_3^-$ -N)

Nitrate nitrogen is reduced to nitrite in a strongly alkaline solution by hydrazine sulphate under the catalytic effect of  $\text{Cu}^{++}$ , and nitrite is then determined by method of BENDSCHNEIDER and ROBINSON [4].

### 2.2.4. DISSOLVED ORGANIC NITROGEN (DON)

The concentration of the dissolved organic nitrogen was determined as the difference between the concentrations of nitrogen forms measured by the Kjeldahl method and the concentration of ammonium nitrogen in the water samples when filtered through a Synpor membrane filter with pore diameter 0.4  $\mu\text{m}$ .

#### 2.2.5. TOTAL ORGANIC NITROGEN (TON)

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

#### 2.2.6. PARTICULATE ORGANIC NITROGEN (PON)

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

#### 2.2.7. TOTAL NITROGEN (TN)

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

### 2.3. EXPERIMENTAL RESULTS

The experimental data on the nitrogen transformation at 18°C in the water withdrawn from the Sližava Reservoir on 24 October 1979, 11 February 1980, and 26 April 1980, are shown in tables 1-3. The water samples in experiments 1, 4, and 7, without the addition of nitrogen compounds, served as controls for the following analysis. All data show that there is a marked difference both in the concentrations of all the nitrogen fractions in the water samples taken from the Sližava Reservoir in the different month and in the development of nitrification under various experimental conditions. The results in tables 1-3 allow also to assume that the ammonium oxidation rates at 18°C without any addition of inorganic forms of nitrogen (experiments 1, 4, and 7) are dependent on the time of sampling during the year. These rates are the slowest in the February sample (experiment 4), when more than 50% of the initial amount of  $\text{NH}_4^+\text{-N}$  still remains in the water after 17 days of incubation. On the other hand, in the October sample (experiment 1), only 14% of ammonium nitrogen was found after 8 days of incubation.

It is generally supposed that there is a marked correlation between the ammonium nitrogen decrease and the increase of nitrite nitrogen 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 and nitrite nitrogen, 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 4), when the nitrite-N peak was around the 9th day; in the April sample (experiment 7), this peak occurred on the 7th day, and in the October sample (experiment 1) on 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 on the 35th

Table 1

Changes of nitrogen compound concentrations (in mg N/dm<sup>3</sup>) at 18° C for water samples from the Sliřava Reservoir (sampling date 24 X 1979)

Zmiany stężeń związków azotowych w próbkach wody pobranych ze zbiornika Sliřava w temperaturze 18° C, wyrażone w mg N/dm<sup>3</sup> (data poboru próbek 24 X 1979)

Experiment No.	Nitrogen fractions	Days of water exposition							
		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 <sub>4</sub> <sup>+</sup> -N	1.80	0.254	0.015	0.5	0.01	0.006	0.031	0.022
	NO <sub>2</sub> <sup>-</sup> -N	0.021	1.09	0.19	0.011	0.002	0.002	0.005	0.005
	NO <sub>3</sub> <sup>-</sup> -N	0.049	0.512	2.24	2.06	2.05	2.07	2.10	2.32
	TN	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 <sub>4</sub> <sup>+</sup> -N	4.35	3.44	0.25	0.19	0.15	0.09	0.051	0.075
	NO <sub>2</sub> <sup>-</sup> -N	0.072	1.09	2.42	0.004	0.004	0.005	0.005	0.005
	NO <sub>3</sub> <sup>-</sup> -N	0.40	1.18	2.32	3.19	3.83	3.62	3.86	3.93
	TN	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 <sub>4</sub> <sup>+</sup> -N	30.3	30.6	0.39	0.15	0.04	0.054	0.041	0.15
	NO <sub>2</sub> <sup>-</sup> -N	0.34	1.28	4.35	0.007	0.007	0.007	0.009	0.009
	NO <sub>3</sub> <sup>-</sup> -N	1.15	2.14	15.1	20.3	20.2	21.1	21.8	22.2
	TN	33.39	36.72	31.14	30.71	31.65	30.70	29.31	28.01

day. In February it must have been later than the 38 th day, i.e. after the end of the experiment.

The addition of mineral forms of nitrogen to the water samples used for experiments caused only slight changes in the rate of the nitrification process, as shown in tab. 1 for October, tab. 2 for February, and tab. 3 for April. For instance, by comparing the experimental results obtained in April, the nitrite nitrogen peak was reached on the 7th day in water samples with total nitrogen content adjusted to 10 or 23 mg/dm<sup>3</sup> and with the control samples having 4.6 mg N/dm<sup>3</sup>. It seems that the various levels of total nitrogen in the system have only a limited influence on the initial rate of ammonium nitrogen 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.

The organic nitrogen content during experiments was rather unstable. With water samples taken from the reservoir in February or April, the total organic nitrogen concentra-

Table 2

Changes of nitrogen compound concentrations (in mg N/dm<sup>3</sup>) at 18°C for water samples from the Slřava Reservoir (sampling date 11 II 1980)

Zmiany stężeń związków azotowych w próbkach wody pobranych ze zbiornika Slřava w temperaturze 18°C, wyrażone w mg N/dm<sup>3</sup> (data poboru próbek 11 II 1980)

Experiment No.	Nitrogen fractions	Days of water exposition						
		0	2	9	17	23	30	38
4	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 <sub>4</sub> <sup>+</sup> -N	0.30	0.22	0.19	0.17	0.02	0.02	0.02
	NO <sub>2</sub> <sup>-</sup> -N	0.014	0.019	0.17	0.025	0.003	0.002	0.005
	NO <sub>3</sub> <sup>-</sup> -N	1.09	1.10	0.93	2.21	2.40	2.55	2.67
	TN	2.93	2.92	2.80	3.10	2.84	2.89	2.89
5	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 <sub>4</sub> <sup>+</sup> -N	3.20	3.09	3.40	0.60	0.005	0.020	0.010
	NO <sub>2</sub> <sup>-</sup> -N	0.147	0.13	0.32	0.02	0.02	0.01	0.01
	NO <sub>3</sub> <sup>-</sup> -N	2.13	2.05	2.88	5.80	6.30	6.80	6.73
	TN	7.01	7.36	7.64	7.97	7.22	7.65	7.43
6	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 <sub>4</sub> <sup>+</sup> -N	12.3	11.2	12.6	1.52	0.01	0.04	0.01
	NO <sub>2</sub> <sup>-</sup> -N	0.55	0.80	0.67	0.70	0.003	0.013	0.005
	NO <sub>3</sub> <sup>-</sup> -N	2.25	2.10	2.67	14.8	15.5	15.4	15.33
	TN	16.63	17.76	18.94	19.22	17.90	16.76	15.88

tion was considerably decreased by the end of the experiments. Practically in all cases we have observed a direct connection between the decrease of the total and particulate 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 cannot be taken into account quantitatively during sampling which results in the lowered levels of individual nitrogen fractions as well as total nitrogen. This methodological error leads to some deviation in the sum of total nitrogen content in the experimental systems. In any case these deviations do not exceed  $\pm 15\%$  of the arithmetical mean; therefore this value may be considered as an upper limit of analytical error. According to experimental conditions, the given systems are virtually closed ones 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 con-

Table 3

Changes of nitrogen compound concentrations (in mg N/dm<sup>3</sup>) at 18°C for water samples from the Sliava Reservoir (sampling date 26 IV 1980)

Zmiany stężeń związków azotowych w próbkach wody pobranych ze zbiornika Sliava w temperaturze 18°C, wyrażone w mg N/dm<sup>3</sup> (data poboru próbek 26 IV 1980)

Experiment No.	Nitrogen fractions	Days of water exposition						
		0	7	21	28	35	43	50
7	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 <sub>4</sub> <sup>+</sup> -N	0.34	0.36	0.005	0.005	0.005	0.005	—
	NO <sub>2</sub> <sup>-</sup> -N	0.03	0.17	0.002	0.010	0.005	0.002	—
	NO <sub>3</sub> <sup>-</sup> -N	2.13	2.12	3.13	3.39	4.67	4.56	—
	TN	4.67	4.63	4.66	4.62	5.12	5.16	—
8	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 <sub>4</sub> <sup>+</sup> -N	4.73	3.94	0.02	0.005	0.005	0.005	—
	NO <sub>2</sub> <sup>-</sup> -N	0.15	0.79	0.002	0.002	0.002	0.002	—
	NO <sub>3</sub> <sup>-</sup> -N	2.20	2.95	7.22	10.18	10.15	10.35	—
	TN	10.91	10.71	9.90	10.89	10.66	10.93	—
9	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 <sub>4</sub> <sup>+</sup> -N	14.82	15.69	1.55	1.78	1.52	1.64	1.78
	NO <sub>2</sub> <sup>-</sup> -N	0.72	1.34	0.02	0.04	0.005	0.005	0.005
	NO <sub>3</sub> <sup>-</sup> -N	2.53	4.39	15.99	18.45	18.63	18.83	18.96
	TN	23.37	25.93	23.48	21.83	21.81	22.22	22.65

clude that the water from the Sliava 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 modelling.

### 3. MATHEMATICAL SIMULATIONS

#### 3.1. MATHEMATICAL MODEL OF NITROGEN TRANSFORMATION

The detailed description of the mathematical model used in the present paper is given by LEONOV [11]. Figure 2 illustrates the interrelationships between the compartments considered in the model.

As obvious from fig. 2, the model includes the main nitrogen compounds measured in the experiments, such as ammonium nitrogen ( $\text{NH}_4^+\text{-N}$ ), nitrite nitrogen ( $\text{NO}_2^-\text{-N}$ ), nitrate nitrogen ( $\text{NO}_3^-\text{-N}$ ), dissolved organic nitrogen (DON), and particulate organic nitrogen (PON).

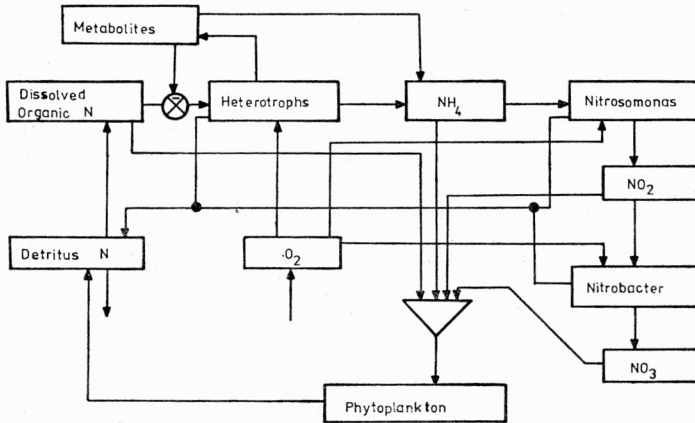


Fig. 2. Components of the nitrogen transformation model and their interrelationships  
Rys. 2. Składniki modelu przemian azotu i ich współzależności

The model was used for analysis of the dynamics of the nitrogen compounds in experimental dark conditions, i.e. without photosynthetic production of organic matter. The following ecological processes are considered important in nitrogen transformation under given conditions:

- growth of heterotrophs transforming DON to  $\text{NH}_4^+\text{-N}$ ,
- growth of *Nitrosomonas* transforming  $\text{NH}_4^+\text{-N}$  to  $\text{NO}_2^-\text{-N}$ ,
- growth of *Nitrobacter* transforming  $\text{NO}_2^-\text{-N}$  to  $\text{NO}_3^-\text{-N}$ ,
- decomposition of organic nitrogen bound to the phytoplankton biomass,
- formation of detritus nitrogen and its decomposition to DON.

The bacterial uptake of nutrients is described by Langmuir-Hinshelwood equations, where the uptake rate is a function of water temperature and nutrient concentration. The rates of metabolite excretion by microorganisms are given by function of specific uptake rates with excretion activities that are different for each type of microorganism. 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. Oxygen is introduced in the model as an important water quality characteristics dependent on the nitrogen transformation. Mathematical expressions used in this model, as well as initial values of all nitrogen forms and rate constants, are presented in a special report [10]. In the model runs, similar values of rate coefficients were used for the simulation of nitrogen dynamics observed in experiments.



3.2. COMPARISON OF OBSERVED AND SIMULATED DATA

Figures 3-11 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 quantitatively describes the major tendencies in concentration changes of nitrogen forms measured in the experiments. From visual comparison of experimental and modelling 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 modelling data, so that the best agreement is achieved at the lowest nitrogen concentrations, while with increasing nitrogen levels, 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

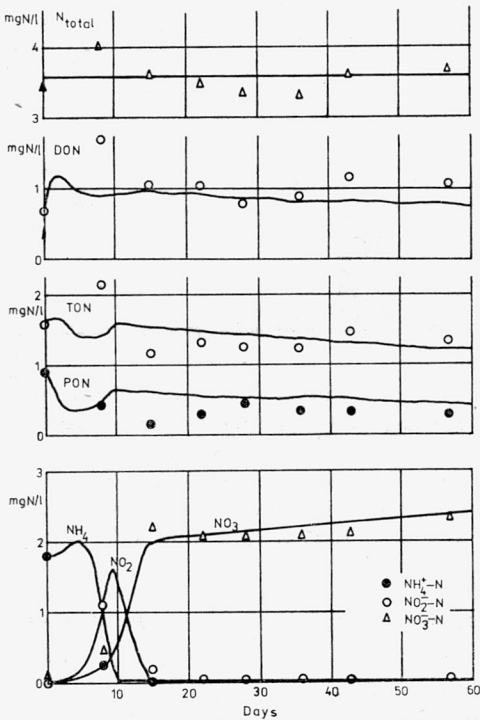


Fig. 3. Comparison of simulation results (curves) with observations in experiment 1 (points)

Rys. 3. Porównanie wyników symulacyjnych (krzywe) z wynikami pomiarowymi uzyskanymi podczas eksperymentu 1 (punkty)

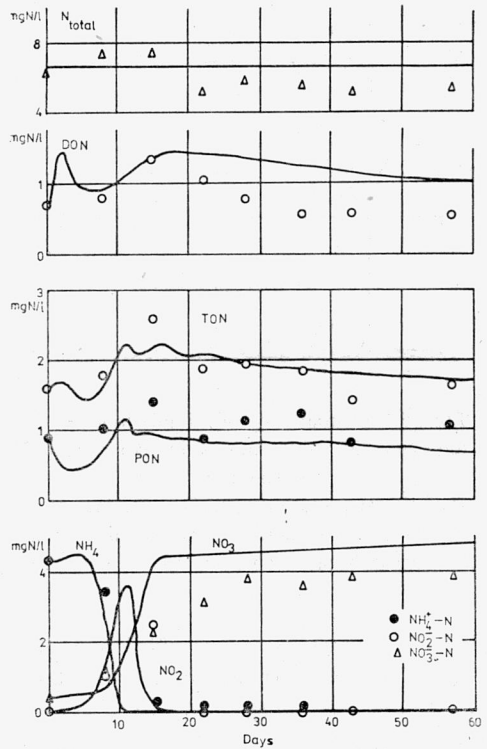


Fig. 4. Comparison of simulation results (curves) with observations in experiment 2 (points)

Rys. 4. Porównanie wyników symulacyjnych (krzywe) z wynikami pomiarowymi uzyskanymi podczas eksperymentu 2 (punkty)

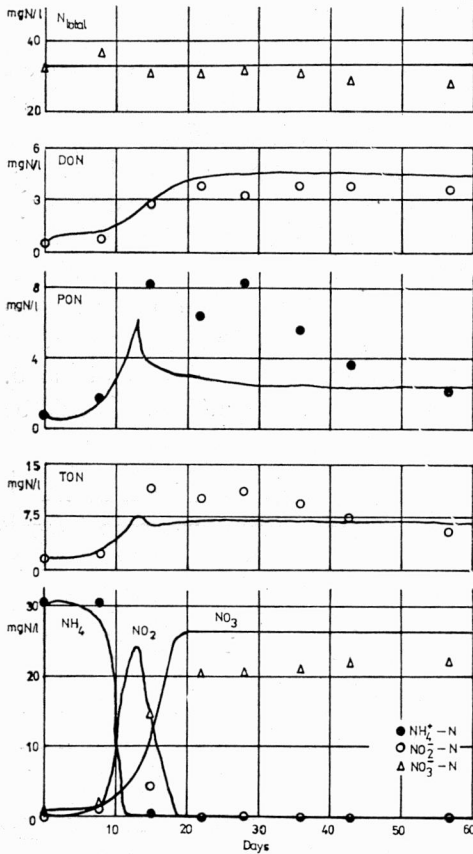


Fig. 5. Comparison of simulation results (curves) with observations in experiment 3 (points)

Rys. 5. Porównanie wyników symulacyjnych (krzywe) z wynikami pomiarowymi uzyskanymi podczas eksperymentu 3 (punkty)

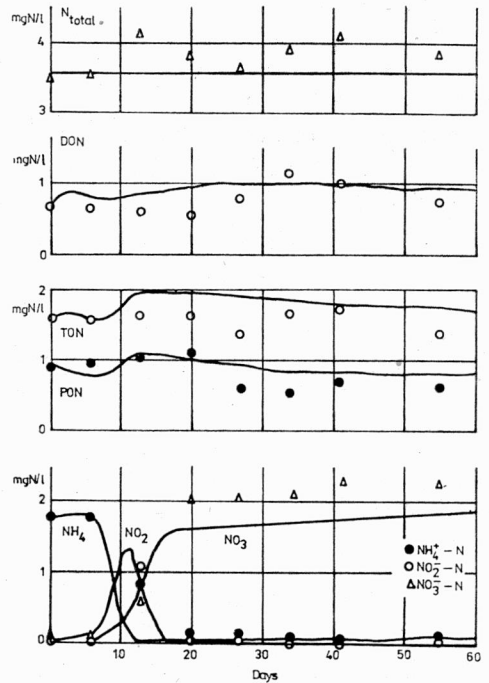


Fig. 6. Comparison of simulation results (curves) with observations in experiment 4 (points)

Rys. 6. Porównanie wyników symulacyjnych (krzywe) z wynikami pomiarowymi uzyskanymi podczas eksperymentu 4 (punkty)

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 relatively high nitrite level, due to active phases of nitrification that shows the difficulty in choosing the proper time step between measurements in order to find the nitrite nitrogen dynamics. From the experimental results, it is obvious that periods of nitrite nitrogen increase and their peaks were not detected by measurement and as a result of this, the major part of experimentally measured nitrite nitrogen concentrations are lower than those obtained by modelling. Slightly higher experimental values in comparison with those simulated by the model can be found for the ammonium nitrogen and for the final levels of the nitrate nitrogen. This is also the case for a few results of various forms of organic nitrogen. Finally, it is possible to assume that in most cases, there are no sub-

stantial differences between experimental and simulated results for other nitrogen forms such as DON, TON, and TN.

A quantitative assessment of how the modelling results agree with observed nitrogen dynamics was made by statistical methods [1, 2]. Comparison of mean nitrogen concentrations calculated on the basis of measurements and simulations allows one to conclude that mean values of all nitrogen forms (DON, PON, TON,  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_2^-\text{-N}$ ,  $\text{NO}_3^-\text{-N}$ , TN) are not higher than the possible analytical error ( $\pm 15\%$ ) and both observed and computed nitrogen values represent a similar population. Analysis of variances for observed and computed nitrogen forms based on an F-test [2] shows that variances of mean in both series of data are homogenous for each form of nitrogen in all experiments. The exclusion

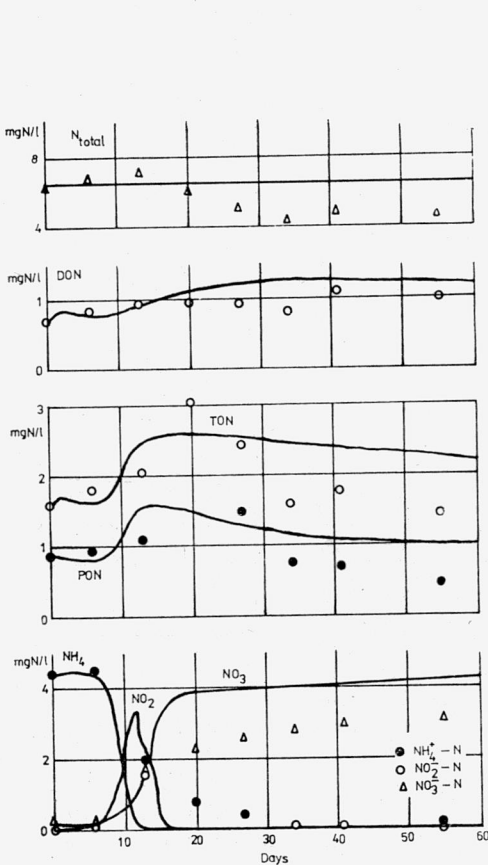


Fig. 7. Comparison of simulation results (curves) with observations in experiment 5 (points)

Rys. 7. Porównanie wyników symulacyjnych (krzywe) z wynikami pomiarowymi uzyskanymi podczas eksperymentu 5 (punkty)

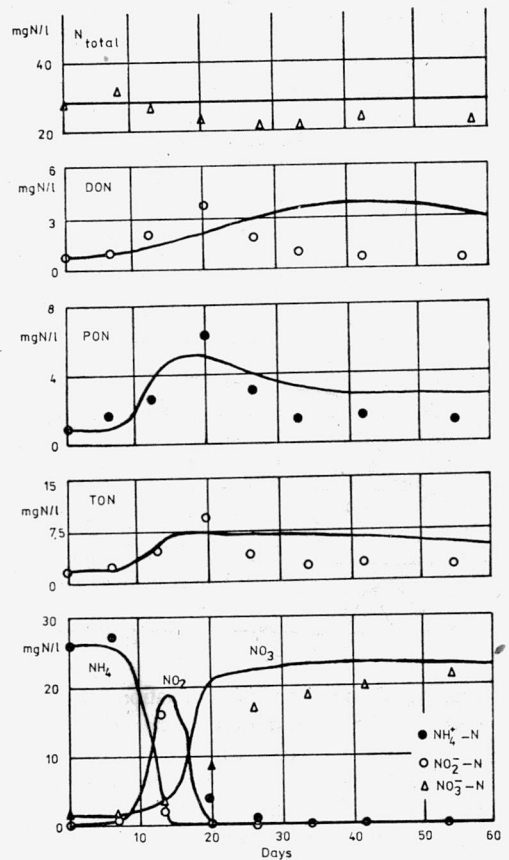


Fig. 8. Comparison of simulation results (curves) with observations in experiment 6 (points)

Rys. 8. Porównanie wyników symulacyjnych (krzywe) z wynikami pomiarowymi uzyskanymi podczas eksperymentu 6 (punkty)

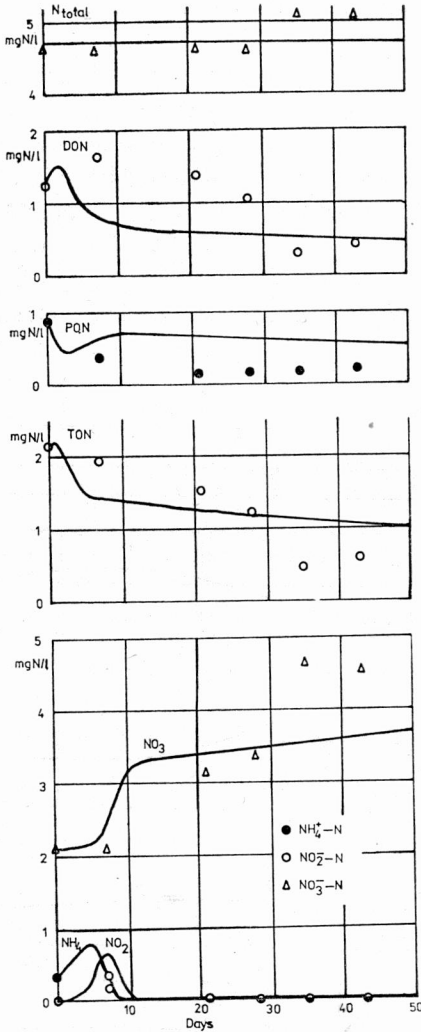


Fig. 9. Comparison of simulation results (curves) with observations in experiment 7 (points)

Rys. 9. Porównanie wyników symulacyjnych (krzywe) z wynikami pomiarowymi uzyskanymi podczas eksperymentu 7 (punkty)

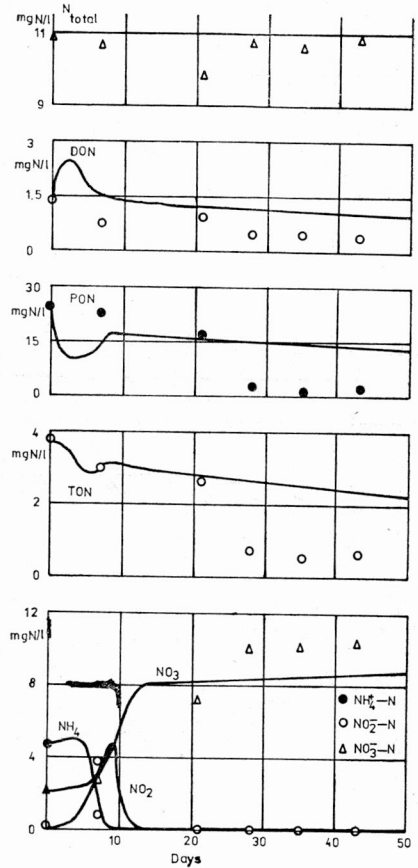


Fig. 10. Comparison of simulation results (curves) with observations in experiment 8 (points)

Rys. 10. Porównanie wyników symulacyjnych (krzywe) z wynikami pomiarowymi uzyskanymi podczas eksperymentu 8 (punkty)

may be done for variances of PON in experiments 3 and 6 (i.e. where nitrogen levels were the highest) and for variances of nitrite nitrogen in experiments 3, 5 and 7-9. However, both of these nitrogen forms are measured with limited accuracy because of the analytical difficulty (for PON) and the rapid concentration changes during active nitrification phase (for nitrite nitrogen).

For the quantitative relationship between observed and simulated nitrogen concentrations, a standard linear regression was computed. It shows a high correlation with a regression line slope close to 1 (excluding  $b = 0.615$  for DON and  $b = 0.249$  for  $\text{NO}_2^-$ -N). High significant values of  $t$  ratio in  $b$  estimations show that the linear relationship between both data is rather representative and the hypothesis that  $b = 0$  would be rejected at 5% level of significance.

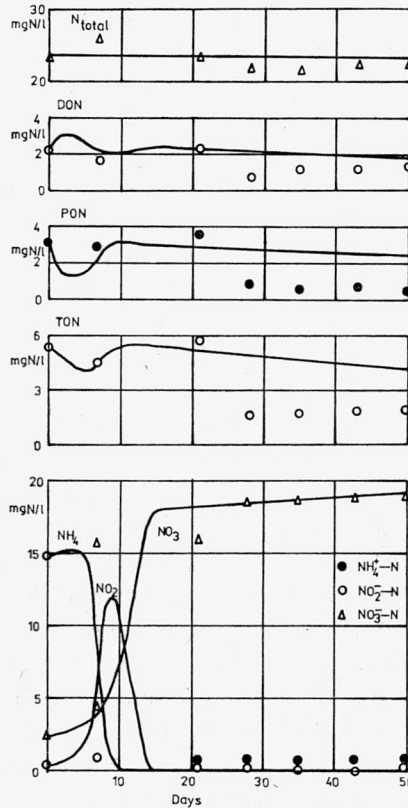


Fig. 11. Comparison of simulation results (curves) with observations in experiment 9 (points)  
Rys. 11. Porównanie wyników symulacyjnych (krzywe) z wynikami pomiarowymi uzyskanymi podczas eksperymentu 9 (punkty)

Values of  $r^2$  for the relationship between observed and simulated nitrogen values lie in the range of 0.43, 0.53, 0.62, 0.68, 0.89, 0.93, and 0.96 for PON, DON, TON,  $\text{NO}_2^-$ -N,  $\text{NH}_4^+$ -N,  $\text{NO}_3^-$ -N, and total N, respectively, while for samples generalized for all experiments,  $r^2$  is in the range of 0.87-0.96. The mean value of  $r^2$  for all the data is estimated to be equal to 0.932 [10].

### 3.3. ANALYSIS OF THE SIMULATED RESULTS

Many of the important characteristics of nitrogen transformation processes such as bacterial activity and biochemical oxygen consumption 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.

According to simulation results, the bacterial activities in nitrogen transformation may be evaluated in at least two ways. The first one is based on consideration of bacterial excretion. Evaluation of excretion activities of heterotrophs and nitrifiers as obtained from the given model show that variation in changing the excretion activity of each type of bacteria during their growth phase is similar in the different experiments and depends primarily on the initial concentration of substrate taken up in bacterial growth. The excretion activity of nitrifiers is significantly different in the various experiments as a result of widely different initial concentrations of the substrates, ammonium nitrogen and nitrite nitrogen, taken up by *Nitrosomonas* and *Nitrobacter*, respectively. It is the largest in the lag phase and 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, is spent on the construction of biomass, and the remainder part is excreted to water environment in a transformed form. In the logarithmic growth phase, the excretion activity of nitrifiers varies in an even larger range: from 0.3 to 0.88 for *Nitrosomonas* and from 0.29 to 0.98 for *Nitrobacter*, while during the mortality growth phase it is equal to 0.29-0.49 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.

The oxidative potential of bacteria, which is the second criteria of bacterial activity considered in this study, was calculated as a product of the specific rate of substrate uptake and the bacterial biomass at any given time moment. The highest values of the oxidative potential for *Nitrosomonas* (9.8-12.0 mg N/dm<sup>3</sup>-day) were estimated for experiments 3 and 9 where a high initial concentration of ammonium nitrogen (30.3 and 14.8 mg N/dm<sup>3</sup>, respectively) was available. At an initial ammonium nitrogen concentration of 0.3-4.7 mg N/dm<sup>3</sup> (in experiments 1, 2, 4, 5, 7 and 8), the values of *Nitrosomonas* oxidative potential were significantly lower and equal to 0.4-2.1 mg N/dm<sup>3</sup>-day. The maximum oxidative activity of *Nitrobacter* was estimated equal to 2.9-5.0 mg N/dm<sup>3</sup>-day in experiments 3, 6 and 9 with initial nitrite nitrogen contents of 0.34-0.72 mg N/dm<sup>3</sup>.

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 and the specific rates of substrate uptake by bacteria, these values can be reproduced by the model to a certain degree of accuracy only when the experimental data on the dynamics of biomass population changes are available.

One of the important problems in water quality studies is evaluation of the influence of nitrogen transformation processes on the oxygen balance. The model considered in this report provides an opportunity to assess the dynamics of oxygen as a result of nitrogen

Table 4

Review of rate coefficients used for description of bacterial growth in nitrogen transformation models  
Przegląd współczynników szybkości reakcji stosowanych do opisu wzrostu bakteryjnego w modelach przemian azotu

Experimental observations	Type of water	Temperature, °C	Mathematical modelling					Reference
			Bacteria	Initial bacterial biomass, mg N/dm <sup>3</sup>	K <sub>M</sub> , mg N/dm <sup>3</sup>	μ, day <sup>-1</sup>	Y	
7	river	18-19	<i>Nitrosomonas</i>	0.02-0.1	0.2-8.0	0.2-2.1	0.05	[9]
			<i>Nitrobacter</i>	0.01-0.1	0.2-8.0	0.5-2.5	0.01	[9]
			<i>Nitrosomonas</i>	0.05	0.06	0.7-1.2	0.05	[8]
			<i>Nitrobacter</i>	0.02	1.7	1.1-1.8	0.02	[8]
			<i>Nitrosomonas</i>	0.0015	0.066	1.11	0.01-0.64	[11]
			<i>Nitrobacter</i>	0.008	0.026	0.517	0.03-0.58	[11]
			<i>Heterotrophs</i>	0.04	0.17-0.19	1.09-2.89	0.38-0.39	[11]
9	sewage	23±1	<i>Nitrosomonas</i>	6.1	0.063	1.08	0.05	[12]
			<i>Nitrobacter</i>	5.5	0.160	1.44	0.02	[12]
	river	—	<i>Nitrifiers</i>	0.01	10.0	0.08	1.0	[14]
			<i>Heterotrophs</i>	10.0	100.0	0.4	0.5	[14]
11	sewage	10-15	<i>Nitrosomonas</i>	5.0	2.5	0.72	0.041	[3]
			<i>Nitrobacter</i>	3.0	1.2	0.93	0.033	[3]
13	sea	18-19	<i>Nitrosomonas</i>	5 × 10 <sup>-7</sup>	0.002	0.495	0.03-0.3	[11]
			<i>Nitrobacter</i>	3 × 10 <sup>-8</sup>	0.002	0.497	0.03-0.93	[11]
			<i>Heterotrophs</i>	1 × 10 <sup>-4</sup>	0.091-0.145	2.47-2.55	0.13-0.3	[11]
14	lake	18-19	<i>Nitrosomonas</i>	4 × 10 <sup>-4</sup>	0.6	1.2	0.05	[8]
			<i>Nitrobacter</i>	7 × 10 <sup>-3</sup>	1.7	1.8	0.02	[8]
			<i>Heterotrophs</i>	1 × 10 <sup>-4</sup>	0.15	1.0	0.2	[8]
			<i>Nitrosomonas</i>	7 × 10 <sup>-4</sup>	0.021-0.058	0.38-0.4	0.06-0.77	[11]
			<i>Nitrobacter</i>	8-8.5 × 10 <sup>-3</sup>	0.04-0.076	0.27-0.28	0.24-0.93	[11]
			<i>Heterotrophs</i>	8 × 10 <sup>-5</sup>	0.17-2.58	2.85-14.1	0.19-0.75	[11]
15	sewage	18-19	<i>Nitrosomonas</i>	0.065	0.053	0.425	0.03-0.48	[11]
			<i>Nitrobacter</i>	0.5	0.035	0.305	0.08-0.41	[11]
			<i>Heterotrophs</i>	0.04	0.2-0.78	0.92-0.96	0.68-0.69	[11]
			<i>Nitrosomonas</i>	—	0.06-5.6	0.46-2.2	0.03-0.13	[13]
			<i>Nitrobacter</i>	—	0.06-8.7	0.28-1.44	0.02-0.08	[13]
			<i>Heterotrophs</i>	—	1-181	7.2-17.0	0.37-0.79	[13]
1	reservoir	18	<i>Nitrosomonas</i>	0.7-3.5 × 10 <sup>-3</sup>	0.099	0.95	0.11-0.71	[10]
			<i>Nitrobacter</i>	0.8-2.0 × 10 <sup>-3</sup>	0.014	0.503	0.02-0.52	[10]
			<i>Heterotrophs</i>	8.0-8.5 × 10 <sup>-4</sup>	2.105	15.54	0.37-0.39	[10]
		12	<i>Nitrosomonas</i>	7 × 10 <sup>-4</sup>	0.139	0.88	0.16-0.74	[10]
			<i>Nitrobacter</i>	8 × 10 <sup>-4</sup>	0.021	0.496	0.03-0.58	[10]
			<i>Heterotrophs</i>	8 × 10 <sup>-5</sup>	2.652	13.83	0.35-0.39	[10]

conversion and to obtain quantitative information on oxygen consumption by different types of bacteria [10].

It is also interesting to compare the values of the rate coefficients as well as initial values of bacterial biomasses used for the description of bacterial growth in nitrogen transformation models. In the given model the changes in bacterial biomasses at each moment of time are defined by differences in the values of specific rates of substrate uptake, the excretion of metabolized products, and mortality. For comparison of the rate coefficients used in this study and those available in the literature, where only uptake and mortality were considered, we must couple the kinetic terms describing bacterial uptake and excretion [10].

Table 4 presents the set of kinetic coefficients and bacterial biomasses in mg N/dm<sup>3</sup> used in modelling the nitrogen transformations. It confirms that the levels of bacterial biomasses applied in this paper, as well as in earlier studies of nitrogen transformations in different water environments [11], correspond well to those evaluated for natural situations [6]. The rate coefficients  $\mu$  and  $K_M$  also agree with the ranges of values quoted in the literature. Simulation results allow for estimation of the changeable values of the yield coefficients,  $Y$ , for different bacterial growth phases. Table 4 also shows the possible ranges of  $Y$  as estimated by the given model in comparison with constant values for  $Y$  available elsewhere in the literature.

#### 4. CONCLUSIONS

The experimental results obtained with water samples taken from the Slňava Reservoir in different months show that the ammonium oxidation rates depend on the sampling date during the year: they are the slowest in the February and the fastest in October. However, the nitrification ability in the water from the Slňava Reservoir can be proved year-round.

Experimental results were used for testing the simulation capability of the nitrogen transformation model to reproduce possible responses of the aquatic system to varying levels of nutrients. The results of this study show that the given model can predict the behaviour of nitrogen compounds for a wide variety of initial nitrogen concentrations: 0.71-2.24 mg N/dm<sup>3</sup> (for DON), 0.3-30.3 mg N/dm<sup>3</sup> (for ammonium-N), 0.014-0.55 mg N/dm<sup>3</sup> (for nitrite -N), 0.049-2.53 mg N/dm<sup>3</sup> (for nitrate-N). These levels of different nitrogen forms may occur in natural waters and in particular in the Slňava Reservoir as a result of its potential pollution.

A statistical correspondence between observed and simulated nitrogen dynamics was found. The given model satisfies at least two criteria of model accuracy: it gives an acceptable agreement with the nitrogen concentrations observed in experiments and it shows the independence of the rate coefficients from the initial concentrations of the nitrogen forms. The model gives a comprehensive explanation of the observed fluctuations in the various nitrogen forms and yields 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 in a state of dynamic equilibrium.

The results of this study show that the model may be used for an ecological analysis of the chemical-biological processes occurring in the Slnava Reservoir.

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TLENOWA PRZEMIANA AZOTU W ŚRODOWISKU WODNYM:  
EKSPERYMENTY I ICH SYMULACJA MATEMATYCZNA

W pracy przedstawiono wyniki badań nad tlenowymi przemianami związków azotowych w wodach zbiornika Slnava, zlokalizowanym na rzece Váh, Czechosłowacja. Procesy nitryfikacji badano w czasie serii dziewięciu eksperymentów. Wyniki badań przeanalizowano za pomocą modelu matematycznego i oceniono przy pomocy analizy statystycznej.

AEROBE UMWANDLUNG VON STICKSTOFF IM GEWÄSSER:  
VERSUCHE UND IHRE MATHEMATISCHE SIMULATION

Dargestellt werden die Ergebnisse der aeroben Umwandlung von Stickstoffverbindungen im Wasser des Staubeckens Slňava/Vah, ČSSR. Der Nitrifikationsverlauf wurde in 9 Versuchsserien untersucht. Die Ergebnisse wurden statistisch und mit Hilfe von mathematischen Modellen ausgewertet.

АЭРОБНЫЙ ОБМЕН АЗОТА В ВОДНОЙ СРЕДЕ:  
ЭКСПЕРИМЕНТЫ И ИХ МАТЕМАТИЧЕСКАЯ ИМИТАЦИЯ

В работе представлены результаты исследований по аэробным обменам азотистых соединений в водах Водохранилища Сильнава, расположенного на реке Вах в Чехословакии. Процессы нитрификации исследовались во время серии девяти экспериментов. Результаты исследований были проанализированы с помощью математической модели и оценены с помощью статистического анализа.