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Spatial distribution and trend change of nitrate in Slovakia during 1968-1993

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ABSTRACT

The nitrate concentrations trends were evaluated on the basis of trend analysis in five sub-basins of the Ondava river basin for 25 - years time series 1968/69 - 1992/93. A rapid decrease of nitrate concentrations in surface waters was observed in four of them after 1989. The decrease resulted mainly from the lower intensity of agricultural production and fertilization in Slovakia due to economic changes. The application of nitrogen fertilizers decreased from 91 kg per ha of agricultural land (mean for Slovakia) in 1989 to 62 kg per ha in 1991. Therefore, the decrease of nitrate concentrations observed in research basins is expected to occur in other agricultural basins as well. Due to continuing changes in agriculture it is difficult to estimate the trends for next few years but probably the decreasing trend will turn again.

In the second part of the paper statistical analysis of measured daily nitrate concentrations was done. The coefficients of theoretical log-normal curves of non-exceedance of the nitrate concentrations were derived in the studied sub-catchments. Both mean annual and characteristic values of nitrate concentrations derived from daily samples were compared to those estimated from regular monthly samplings of hydrometeorological network. Important differences in the estimates of the characteristic values were found between both approaches.

INTRODUCTION

The deterioration of surface water quality in the last decades is typical for most of the industrial regions. Also the high intensity of agricultural production results in lower water quality. The tendency for self-suffiencyc Kendall test for the statistical analysis of water pollution trends from 403 stations and 27 parameters for 1978-87 in the Continental United States. They found, that the common ions and nutrients have mostly upward trends. The transport processes in streams related to land use were studied by Bowden et al. (1991), Ferguson (1986), and Hakamata et al. (1991). Vrba and Skořepa (1986) estimated the nitrate contents in groundwater since 1981, and Pelikán studied the nitrate concentrations in Moravian rivers in 1963-88. Nesměrák (1986a, 1986b) modelled nitrate washout as related to the runoff depths. He also elaborated the state standard ČSN 75 7221 "Classification of surface water quality" which is valid also for Slovakia since 1990.

In Slovakia the unfavourable influence of agricultural production on water quality was studied by Lichvár (1986). Hanzlíková and Büchlerová (1981) estimated the development of water quality in Velká Domaša reservoir basin and they processed the mean water quality parameters for last 30 years. This area is also corresponding to our investigations.

In our institute Babiaková and Palkovič (1992) were dealing with the accummulation of sulfates and nitrates in snow cover and Rončák and Koníček (1992) studied the nitrates in selected research basins of central Slovakia. Mendel and Pekárová (1993), Mendel and Halmová (1993), Pekárová and Pekár (1993), and Pekárová and Halmová (1994) were dealing with the possibilities of nitrate concentration modelling related to discharges

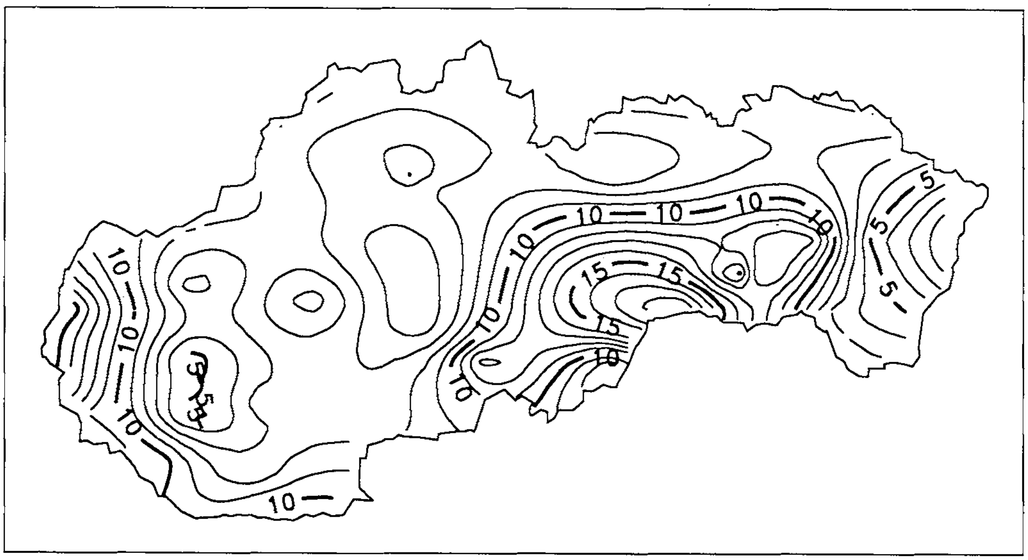


Figure 1. Spatial distribution of nitrates (mg l^{-1}) in surface water in Slovakia in 1989

and the forecasting of the concentrations.

The monitoring of the precipitation, surface and ground water quality is organized by the Slovak Hydrometeorological Institute. According to the data from selected 51 profiles in Slovakia the mean annual nitrate concentration in stream water was 9.7 mgl-1 in 1989 (SHMI, 1989). The maximum value occurred was 19.0 mgl-1 and the minimum one was 4.3 mgl-1.

For the analysis of long-term trends of water pollution the longer time series are needed. Moreover, to study the dynamics of water pollution changes in dependency on other hydrometeorological elements (discharge, temperature, precipitation) we need to know these changes even in time intervals less than 1 day. To study the spatial changes it is also necessary to sample with higher spatial density.

SAMPLING AREA

In order to study the changes of nitrate concentrations in surface flows the regular daily water quality sampling was organized in 5 sub-catchments of the Ondava river basin. The experiment lasted since 1986/87 to 1992/93. Also the measured monthly nitrate concentration series were available in this basin since 1968.

The Ondava river basin is situated in Eastern Slovakia (49o N lat., 22o E long.) in the Ondava hills. The area of the basin in Stropkov profile is 576.5 km2, and the stream length is 55.4 km. The mean elevation of the basin is 450 m a.s.l. The basin is situated in the flysh zone of the Carpathians and the permeability of the geological substrate is characterised as very low. The brown forest soil prevails with beech - oak cover. The climate of the area is characterised as continental with hot summer and cold winter. The mean annual air temperature is 7.5oC,the mean annual precipitation is 752 mm and the runoff coefficient is 0.45. Concerning the surface water pollution by nitrate the basin belongs to relatively clean regions of Slovakia (Fig. 1).

There are no important sources of industrial water pollution in the basin. The only point sources of pollution are the municipal sewerages of Svidník and Stropkov (both less than 15.000 inhabitants). One half of the area is forested, the other one is agricultural area (17% is arable land). On Ondava river 9 km below Stropkov the multi - purpose water reservoir Velká Domaša is in operation since 1970 (total capacity 187.5 mil.m^3, area 14.9 km^2). The possibility of its use for drinking water supply was considered by water authorities. Due to low soil fertility the mean annual doses of NO_3- -N fertilizer were up to 140 kg N ha-1a-1 in 1989.

For the study of spatial and temporal changes of the nitrate concentrations within the Ondava basin 5 subcatchments were chosen. Their basic characteristics are as follows (Table 1). The land use of these catchments is different. The agricultural land use (pasture, arable land) can be expressed as a complement to the forest cover-to-drainage area which is 95%, 60%, 50%, 40% and 9%, respectively.

METHODS

The measured annual series of daily nitrate concentrations were put together in the form of frequency tables. Before selecting the most suitable type of probability distribution curve of nitrate concentrations, several types of probability distribution were tested, mostly used in hydrology: Pearson's of the third type, normal, log-normal, Gumbel's, and Weibull's. The choice of the "best one" for a given series belongs to the classical problems of hydrology and it is not our aim to solve it. For using some of the distribution types it was necessary to take into account a condition that the lower distribution boundary might be a non-negative.

As the studied series have high coefficients of asymmetry, and hold the inequality (1):

$$C_s \geq 3\ C_v$$

where: C_s - coefficient of asymmetry
C_v - coefficient of variation,

the most successful was the use of the three-parametric logarithmic-normal distribution in the form:

$$f(\log(x\text{-}a)) = \frac{1}{\sigma\sqrt{2\pi}} \cdot \frac{1}{x-a} \cdot e^{-\frac{(\log(x\text{-}a)-\mu)^2}{2\sigma^2}}$$

where: x - nitrate concentrations
μ - mean
σ - standard deviation

RESULTS

1. Spatial changes

In order to ascertain the spatial variability of nitrate concentrations and to identify the areas with higher pollution the water quality samples were taken in 72 checking profiles on flows in Ondava basin during 1990-92. The sampling was done in different seasons and different hydrological situations. The checking profiles were selected on both main stream and the tributaries above the Velká Domaša reservoir. The measured data were used for drawing nitrate concentration maps of Ondava basin in different seasons. Using these data also the areas with higher pollution of surface water by nitrates were identified within the basin (Fig. 2).

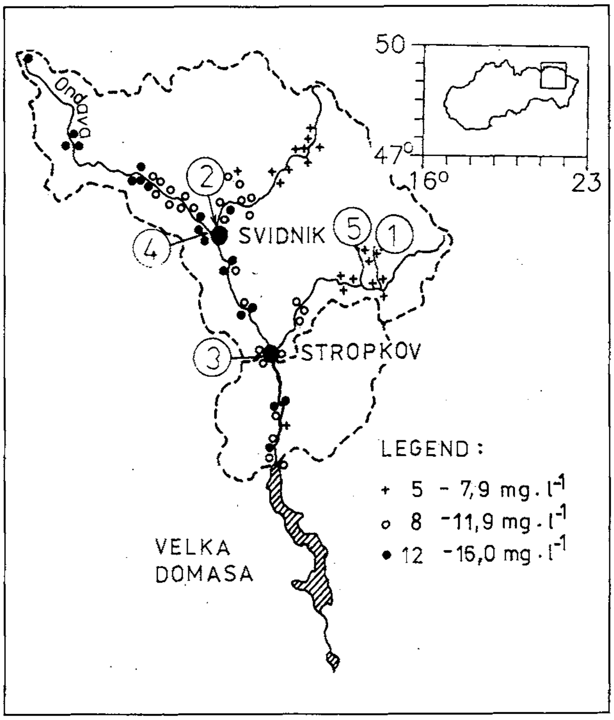


Figure 2. Mean nitrate concentrations in surface water in Ondava basin in 1990-1992. Network stations: 1- Manelo, 2- Ladomírka - svidník, 3- Ondava - Stropkov, 4- Ondava - Svidník, 5- Babie

2. Temporal changes

The water quality samples were taken daily at 6 a.m. during the hydrological years 1986/87 - 1992/93. The mean annual nitrate concentrations in the subcatchments are in Table 2 and the daily nitrate concentrations in cross section 3 are drawn on Fig 3 for seven hydrological years 1986/87 - 1992/93.

3. Trend analysis - smoothing of the monthly nitrate concentration time series

The 25 - years time series of monthly nitrate concentrations in profiles 2, 3 and 4 (see Fig. 2) were processed using trend analysis. On Fig. 4 there we can follow the increase of mean monthly nitrate concentrations in profile 3 Stropkov - Ondava in 1968/69 - 1989/90. The mean annual concentrations increased during 20 years from 2.9 mgl-1 in 1968/69 to 12.8 mgl-1 in 1988/89. After 1988/89 the mean annual nitrate concentration decreased to 5.3 mgl-1 in hydrological year 1992/93.

The simple moving averages method was used for smoothing the monthly nitrates concentration time series. The length of the moving averages was chosen as m = 24. On Fig. 5 there are both original and smoothed data

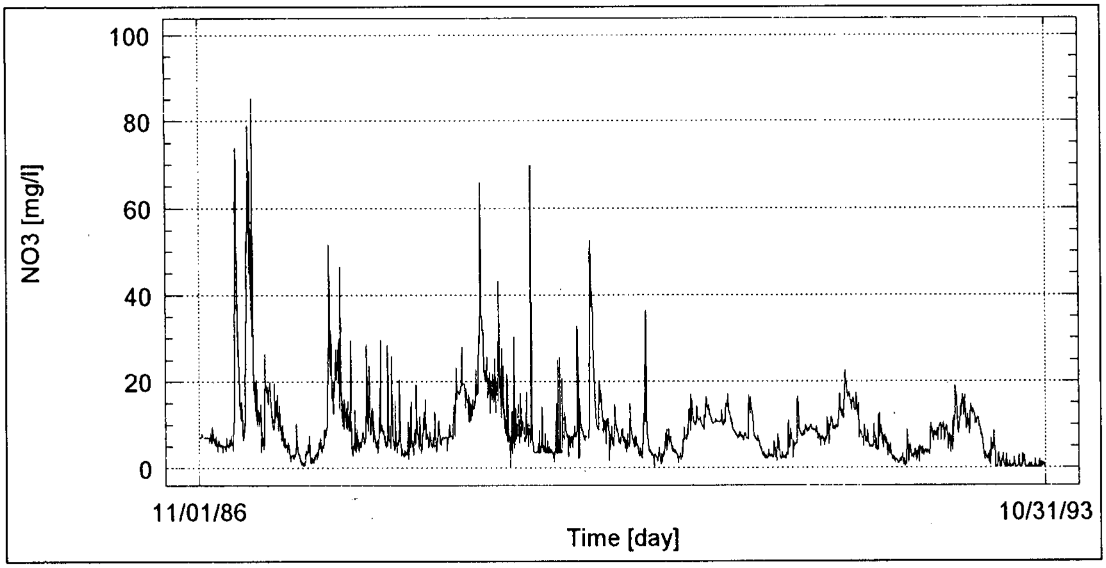


Figure 3. Observed daily nitrate concentrations at Stropkov during seven hydrological years 1986/87 - 1992/93

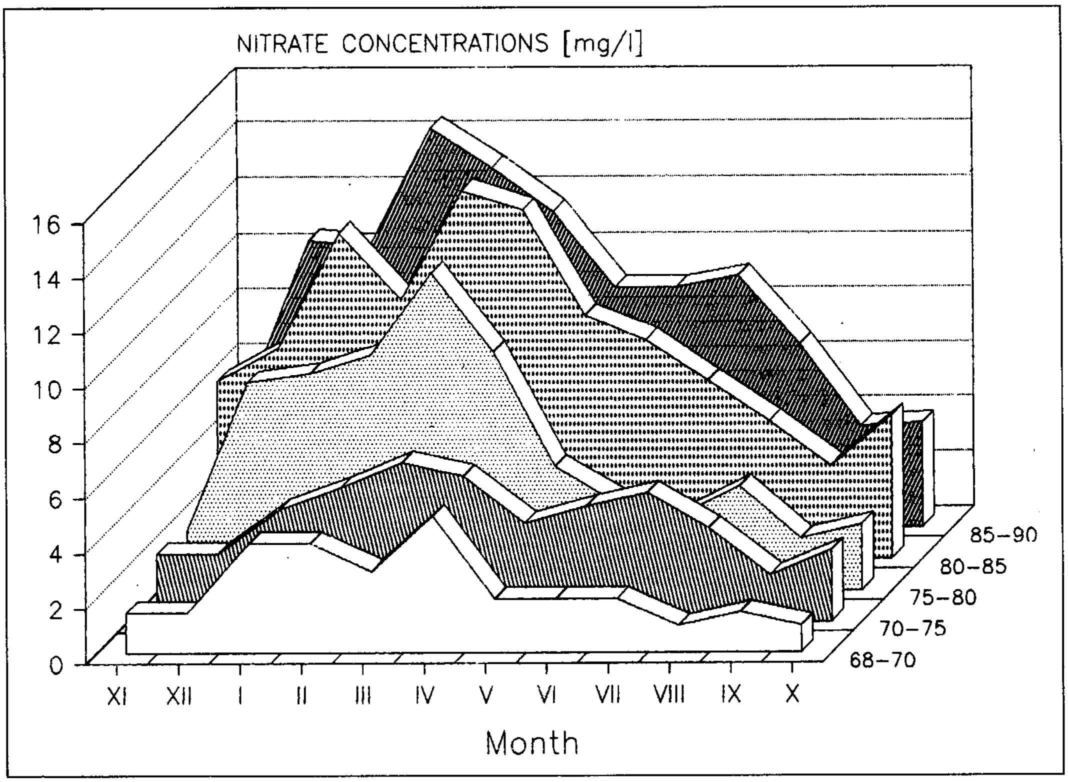


Figure 4. The increase of mean monthly nitrate concentrations at Stropkov in 1968/69 - 1989/90

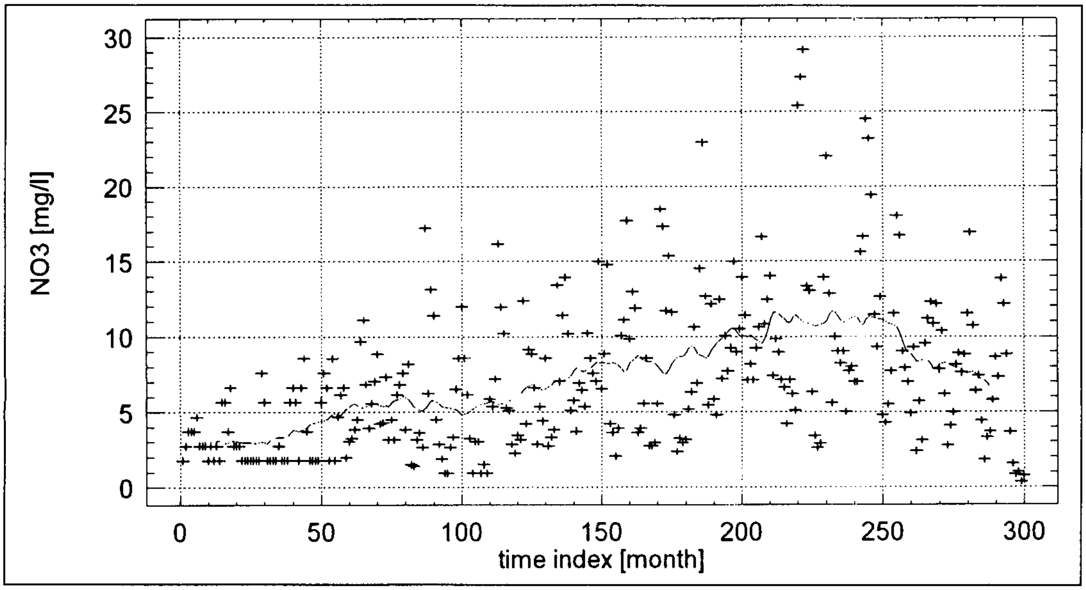


Figure 5. Trend of monthly nitrate concentrations. Measured and smoothed dara from profile 3 Ondava - Stropkov since November 1968 - October 1993

from profile 3. The development of nitrate concentrations in the studied area is also evident from Fig. 5. The concentrations were increasing during 1968/69 - 1986/87, the next four years were stabilized on the highest level and from 1989 onwards concentrations decreased.

4.Testing of daily nitrate concentrations time series - the choice of theoretical curves of the non - exceedance probability of the nitrate concentrations in the streams

In Table 3 there are the basic statistical characteristics of the measured series of daily nitrate concentrations for the six years.

In Figs. 6a - 6f can be visually evaluated an agreement of empirical values and fitted logarithmic-normal curve of distribution for the profile 3 Stropkov - Ondava. For mathematical evaluation of agreement between empirical and theoretical curve of distribution there were used: (2-test, Kolmogorov-Smirnov test and the Romanovsky criterion.

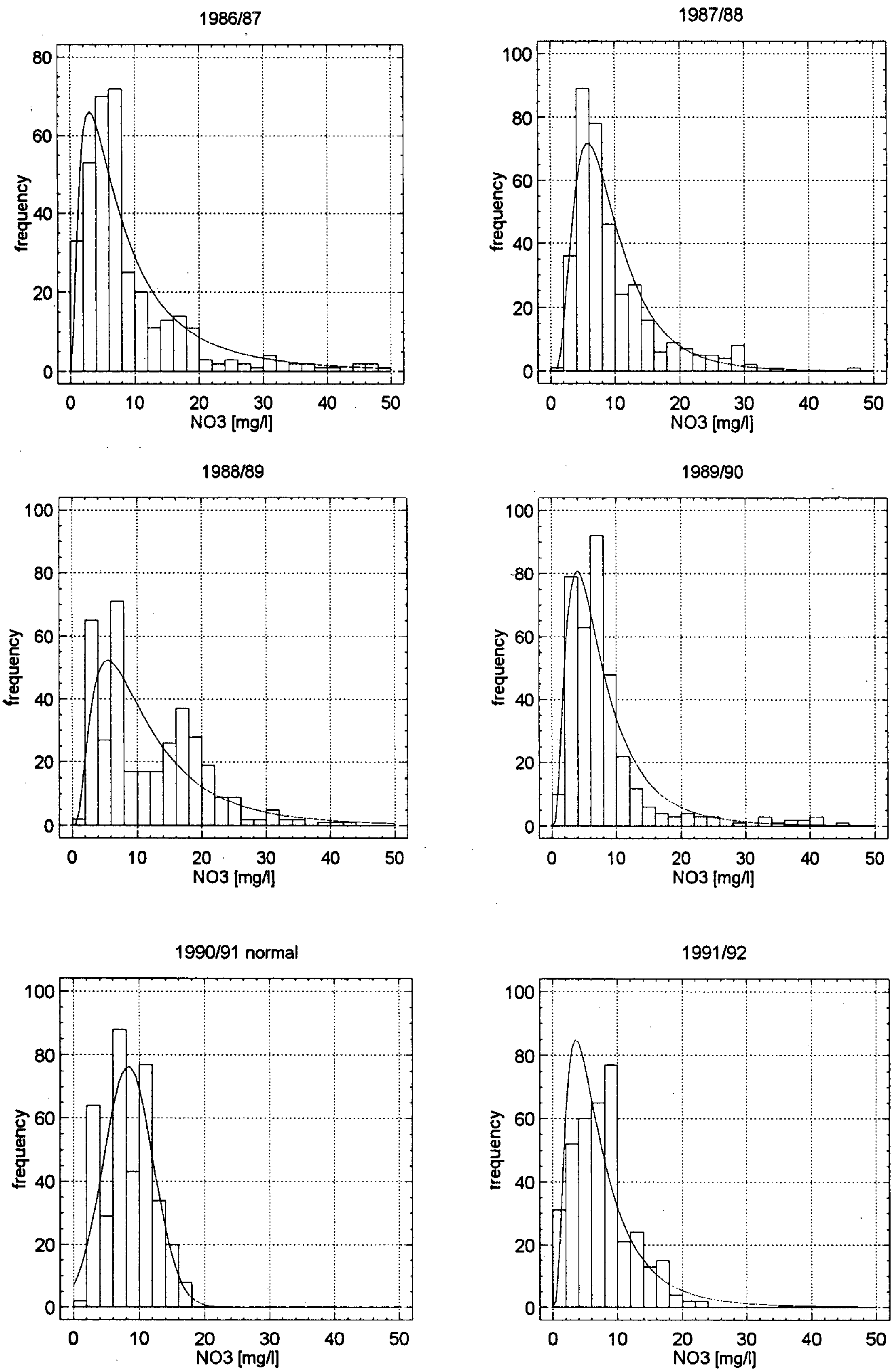
On Fig. 7 there are the empirical curves of non-exceedance of the daily nitrate concentrations in three basins: 1. - forested basin, 3. - mixed land use, 5.- agricultural basin.

The figure shows that most frequently are the higher values of nitrate concentrations exceeded in subbasin 5 Babie - Olšavka. This result is influenced by the fact that the forest-cover-to drainage is the lowest in this basin - 9%, i.e. 91% of the soil is agriculturally exploited.

On the basis of fitted curves of nitrate concentrations exceeedance Table 4 was produced, giving the critical values of nitrate concentrations. There are also the critical values derived from the observed values. The table was elaborated for all five profiles for six years. From Table 4 follows that the 6 - years fitted curves are not suitable for determination of the characteristic values (concentration with probability of non-exceedance 90%) because of the big differencies between corresponding values. The theoretical curves should be estimated for shorter periods which are not influenced by the trend.

By means of non-exceedance curves it is possible to evaluate the water quality in the Ondava river, with regard to nitrates, according to state standard ČSN 75 7221, valid for classification of the quality of surface waters. As a characteristic value is considered the value of concentration with probability of non-exceedance 90% which is calculated from at least 24 values. In the streams intended for drinking purposes (both for inhabitants and animal production), for breeding of salmon-like fish and at special protection of the basin, the 95% of probability non-exceedance is used.

Further, the state standard ČSN 75 7221 establishes the permissible nitrate concentration of up to 15 mg.l-1 for the II. class (pure water) and 50 mg.l-1 for the IV. class.



Figures 6a. 6f. Histograms and theoretical logarithmic-normal (normal) distribution curves for the profile 3 stropkov - Ondava in different hydrological years

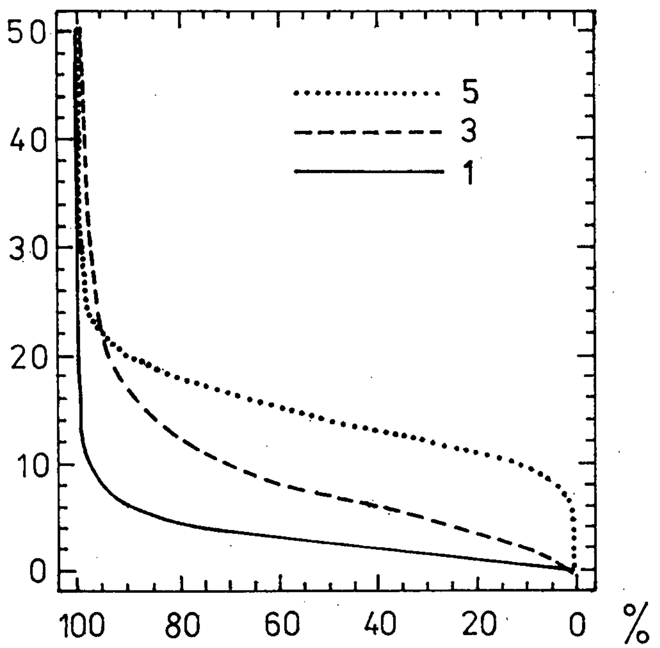


Figure 7. The empirycal curves of non exceedance of the daily nitrate concentrations in different basins (1.- forested, 3.- mixed land use, 5.- Agricultural)

The value of 15 mg.l-1 was, with 95% of probability, not exceeded only in the year 1987/88 in the profile 4 Svidnìk-Ladomìrka. In all other cases it was exceeded. In hydrological year 1988/89 in the profile 4 Svidnìk-Ondava there was exceeded the value of 50 mg.l-1, too.

CONCLUSIONS

The mean annual and characteristic values (values with the probability of non - exceedance 90 % according to the state standard ČSN 75 7221) derived from daily sampling in cross - sections 2, 3 and 4 in 1989 were compared to those derived by Slovak Hydrometeorological Institute in the same cross - sections from monthly sampling (Table 5)

It is obvious that the variability of the daily samples is higher than that of monthly samples. The higher frequency of sampling can discover the extreme values more probably. This assumption is confirmed in Table 5. According to monthly sampling is the upper Ondava river classified into the class II, while according to our data it should be classified as class III..

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Table 1. General characteristics of the five sub-basins

Flow	Profile	Area	Forest	Elevation m a.s.l			Prec	Runoff	
		km^2	%	min	max	mean	mm	mm	coeff.
1. Manelo	Gribov	0.195	95	305	485	383	674	297	0.44
2. Ladomírka	Svidník	185.8	60	225	–	-752	789	404	0.52
3. Ondava	Stropkov	574.0	50	183	543	752	765	345	0.45
4. Ondava	Svidník	167.5	40	225	543	752	747	347	0.46
5. Babie	Olšavka	0.345	9	292	520	406	767	408	0.53

Table 2. Arithmetic mean nitrate concentrations in 5 Ondava sub-basins estimated from measured daily concentrations in mgl-1

Flow	Profile	86/87	87/88	88/89	89/90	90/91	91/92	92/93
Manelo	Gribov	-	3.8	3.9	3.6	3.1	2.6	1.8
Ladomírka	Svidník	14.5	5.6	12.6	9.6	8.1	8.4	6.3
Ondava	Stropkov	11.7	9.9	12.8	8.5	8.3	7.6	5.3
Ondava	Svidník	15.4	7.2	15.3	11.9	9.9	8.6	7.5
Babie	Olšavka	-	16.3	13.7	13.6	14.3	16.4	13.3

Table 3. The basic statistical characteristics of the measured daily nitrate concentrations in 5 sub-catchments for the six hydrological years 1987/88 - 1992/93

sub-catchment number	1.	2.	3.	4.	5.
sample size	2192	2192	2192	2192	2192
mean concentration	3.11	8.44	8.76	10.60	14.60
maximum	24.00	87.40	69.90	135.2	88.00
median	2.40	7.30	7.28	8.72	13.88
modus	0.90	2.00	6.50	1.50	19.00
variation	6.66	46.00	50.72	88.34	28.86
standard deviation	2.58	6.78	7.12	9.40	5.37
standard error	0.06	0.14	0.15	0.22	0.11
coefficient of asymmetry	2.72	3.68	2.68	3.31	4.38
coefficient of variation	0.83	0.83	0.81	0.88	0.36

Table 4. Critical values of nitrate concentrations (mgl-1)

				From fitted curves				From measured values			
№	catchment	m	s	95%	90%	50%	10%	95%	90%	50%	10%
1	Gribov	3.14	2.75	8.1	6.2	2.3	0.9	7.9	6.3	2.4	0.9
2	Svidník	9.54	9.53	26.5	19.6	6.7	2.3	21.0	16.0	7.4	2.4
3	Stropkov	10.6	14.4	33.8	23.0	6.2	1.6	22.3	17.2	7.1	2.6
4	Svidník	11.9	14.3	35.9	25.5	7.6	2.2	27.8	22.3	8.8	1.95
5	Babie	14.7	5.4	24.8	21.1	13.8	8.8	21.9	19.7	13.8	9.8

Table 5. Mean annual and characteristic values c90 of nitrate concentrations (mgl-1) in cross-sections 2, 3 and 4 from monthly network samples (subscript n) and from daily experimental samples - measured (subscript m) and fitted curves (subscript t)

Cross-section	C_n	C_m	C_t	C_{90n}	class	C_{90m}	C_{90t}	class
2-Svidník - Ladomírka.	9.19	12.6	12.6	11.3	II	22.0	24.4	III
3-Stropkov - Ondava	11.2	12.7	13.0	13.7	II	22.4	25.8	III
4-Svidník- Ondava	11.6	15.3	16.7	14.0	II	26.3	27.0	III