DOI: 10.31577/ahs-2020-0021.01.0006

ACTA HYDROLOGICA SLOVACA

Volume 21, No. 1, 2020, 48 – 55

LONG-TERM DEVELOPMENT OF DISCHARGE AND NITRATE CONCENTRATIONS IN THE LITTLE CARPATHIANS HEADWATERS

Pavla Pekárová*, Pavol Miklánek, Ján Pekár, Zuzana Danáčová

One of the requirements imposed by the Water Framework Directive 2000/60/EC (WFD, 2000) is to analyze and predict long-term evolution of surface water quality parameters. During 28-years period (1991–2018), the concentrations of selected pollutants were monitored in the Little Carpathians headwater basins by the Institute of Hydrology, SAS. In this study we analyse the long-term development of runoff and nitrates nitrogen concentrations in the Parná River at Horné Orešany water gauge station during the period 1991–2018. Discharges in the Parná River decreased slightly, but the trend is not statistically significant. In the case of nitrate nitrogen concentrations the marked decrease occurred in this river basin from the value of 5.11 mg l^{-1} during the years 1991–1995 to the value of 2.49 mg l^{-1} in the years 2015–2018. The relation between discharge and nitrate concentration was used to derive exponential empirical relations for estimation of the nitrate nitrogen concentrations in the stream based on mean daily discharge during the sampling day. These equations can be used for indirect estimation of nitrate nitrogen concentrations when they were not measured directly.

KEY WORDS: runoff, discharge variability, nitrate, long term trends

Introduction

One of the negative consequences of the expected global warming will be the increase of stream water temperature and runoff decrease during summer season, which will result in stream water quality worsening. The intensification of the agricultural mass production and increase of the inorganic nitrate fertilization doses worldwide (also in Slovakia) after the Second World War influenced the increase of nitrate concentrations in the stream water. Nitrate loading from an agricultural basin is generally strongly related to the amount of fertilizers applied. On Fig. 1 there is presented the annual development of average consumption of industrial nitrogen fertilizers applied to 1 ha of agricultural soils in Slovakia during the period 1960–2015 (upper). The lower part of the figure shows the monthly nitrate concentrations in three streams with long monitoring (Pekárová and Miklánek, 2013). In the plot we can see the direct influence of the increased nitrate doses upon the nitrate concentrations in the rivers. The fertilizer consumption per hectare arable land in 2012 in other EU countries published by the World Bank (WB, 2020) is plotted in Fig. 2 for comparison. This figure equates to 151 kg of fertilizers consumed per ha arable land on average for the EU countries.

Influence of agricultural activity on the nitrate content in drinking water sources in Slovakia was studied by Hyánková et al (1995). Pavelková (2000) assessed the water quality in drainage channels in the Eastern Slovakian Lowland in 1994–1996. She demonstrated the insufficient water quality, mainly due to nitrites nitrogen concentrations. The long-term development of nitrate in house wells in the villages of Michalovce and Sobrance District was analysed by Pavelková and Babinec (2017). The intensive daily monitoring of nitrate concentrations was managed by IH SAS in 1986–1993 in order to make detailed analysis of nitrate development at the inflow to water reservoir Veľká Domaša. Five sampling sites were established in the Ondava basin, and some other also in the Little Carpathians and Strážov Highland. It was proved by the study that the lowering of fertilisation doses and of the agricultural production resulted in lowering of nitrate concentrations in surface streams (Pekárová and Velísková, 1998; Pekárová and Pekár, 1996; Pekárová and Miklánek, 2013; Velískova et al., 2012). The influence of the forested and arable basin on nitrate concentrations was studied at experimental microbasins of IH SAS near to Kúnovec in the Strážov highland in 1986–2006 (Pekárová et al., 2008). The nitrate concentrations in the small forested Vydrica basin near to Bratislava were studied by Pekárová and Pekár (1998), Pekárová and Onderka (2005), and Sebíň et al. (2007).

The application of fertilizers was at low level in Slovakia in 2012 compared to other EU countries (Fig. 2), but due to increasing fertilization in Slovakia it is necessary to continue in evaluation of the nitrate content in the streams.

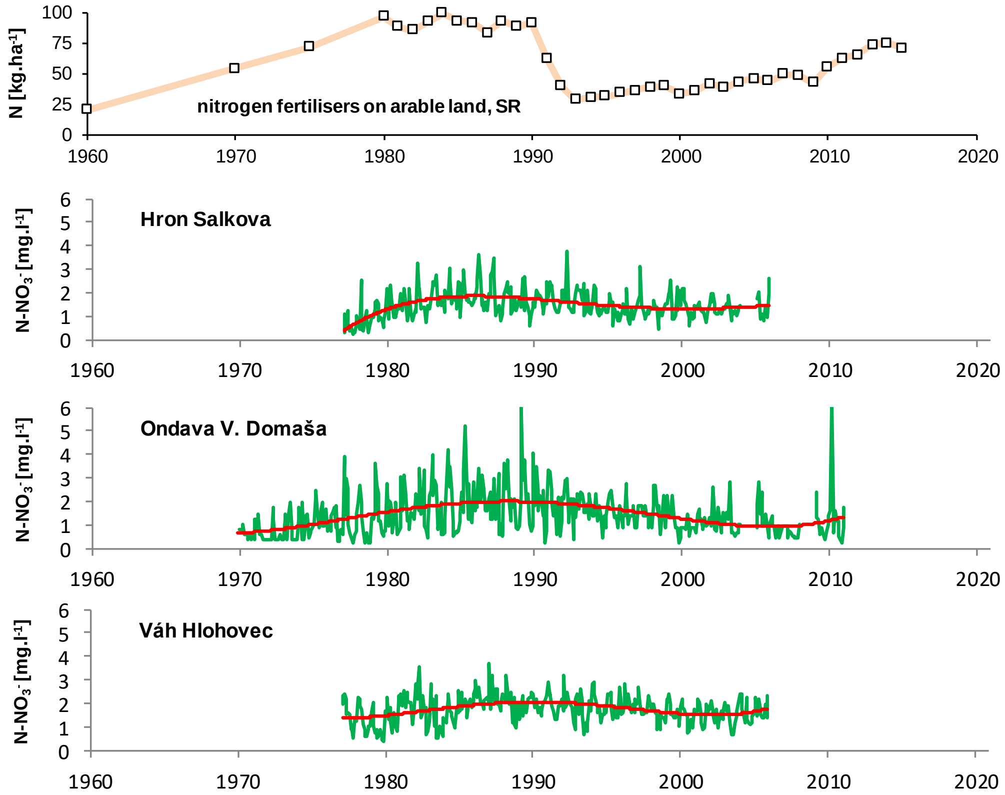


Fig. 1. Annual development of average consumption of industrial nitrogen fertilizers applied to 1 ha of agricultural soils in Slovakia during the period 1960–2015 (upper) in kg per 1 ha of agricultural land. Monthly nitrate nitrogen concentrations of the Hron, Ondava, and Váh rivers (SHMI data, according to Pekárová and Miklánek, 2013).

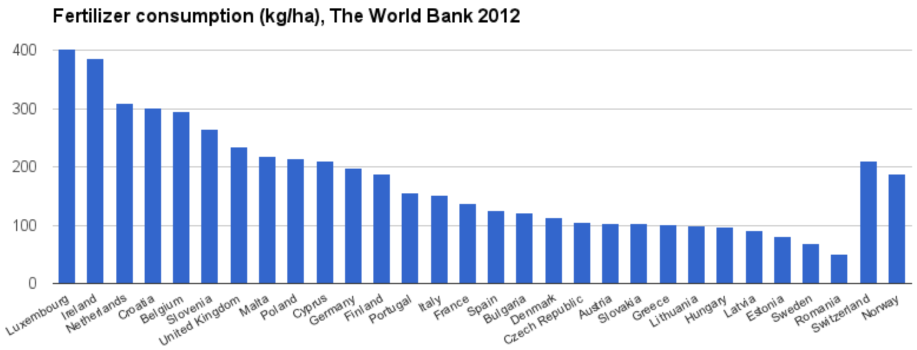


Fig. 2. Fertilizer consumption per hectare arable land in 2012 for the EU countries (the World Bank).

In this study we pay attention to the long-term development of the nitrate concentrations in the Little Carpathians headwater – in the stream Parná during 1991–2018.

The aims of this study are as follows:

1. Detailed analysis of the hydrological regime of the Parná stream at Horné Orešany during 1961–2018;
2. Analysis of the nitrate concentrations observed in the Parná stream at Horné Orešany sampling site in the 28–years period (1991–2018).

Material

The Little Carpathians lie in the Northeast of Bratislava between 17°–17°50' Eastern Longitude and 48°10'–48°40' Northern Latitude. The Little Carpathians are affected by air streams from the agriculturally polluted part of the Western Slovakia and Southern Moravia, which are densely populated areas. Both, the intensive industry and agriculture have a negative influence on water quality in this region. For example, the total volume of waste water discharged from Chemolak Smolenice was 477.3 thousand m^3 in 1991, with BOD_5 of 12.5 t.y^{-1} (tons per year), COD of 38.1 t.y^{-1} and 150.3 t.y^{-1} of insoluble substances (Molnár et al., 1993). The intensive agriculture in the lowland area has great negative impact on high nitrates content in surface water. Most local settlements (incl. Trnava) are exclusively supplied by drinking water from local groundwater sources. Because these sources are irreplaceable, it was necessary to give attention to the water quality problem.

Surface and groundwater quality in the basin of Trnávka River has been studied by several authors in the past. Gálik (1990) was interested in the impact of human activities on groundwater quality. He found that chloride, sulphate, and especially nitrate concentrations increase permanently in the groundwater. Guliš et al. (1994) evaluated drinking water quality. Lehotský and Tóth (1992) assessed the water quality of 96 forest springs and wells on the ridge of the Little Carpathians. Slaninka et al. (2005) monitored precipitation, surface runoff, and spring water runoff, for the sake of mass balance in the Vydrica catchment up to the Spariska section.

The analysis of surface water quality in this study was based on the data obtained by IH SAS at four sampling sites (Fig. 3):

1. Gidra River at water gauge Píla;
2. Parná River at Horné Orešany water gauge;
3. Hlboča brook in Smolenice;
4. Trnávka River at Buková water gauge.

Brief physical and geographical description of these catchments is presented in Table 1.

During last twenty years, surface water samples were taken by Institute of Hydrology, SAS (IH SAS) during three sub-periods: VI 1991–VIII 1995, XI 2004–XII 2006, and IV 2015–XII 2019. During the first period nitrate, nitrite, ammonium, sulphate, phosphate, chloride, and pH were analysed in the chemical laboratory of IH SAS in Michalovce. During second period the samples were analysed in accredited laboratory in Bratislava, and

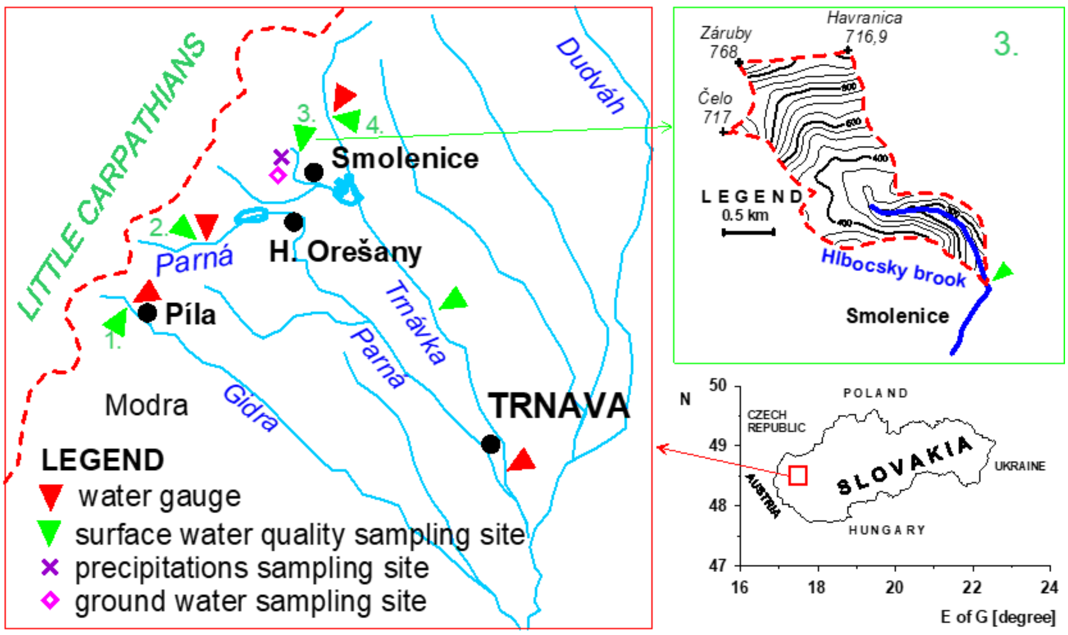


Fig. 3. Location of surface water gauges (SHMI stations) and water quality sampling sites (IH SAS sampling sites) in the Little Carpathians, Hlboča brook basin in details.

Table 1. Basic morphometrical, vegetation, and hydrological characteristics of experimental basins

river - cross-section	area [km^2]	agric. [%]	forest [%]	elev. a.s.l. min	max	G	vegetation
Gidra – Píla	32.95	0	80	280	695	1	beech, oak, hornbeam
Parná – H. Orešany	37.86	10	90	235	661	2	beech, oak, hornbeam
Hlbočský b. – Smolenice	2.31	0	95	240	768	2	beech, oak, hornbeam
Trnávka – Buková	21.88	20	70	220	768	1	beech, oak, hornbeam

G – Characteristics of the geological substrate permeability
1 – good (river sediments), 2 – very good (karst, limestone)

during third period in laboratory of IH SAS in Bratislava. The selected sampling sites of IH SAS represent a head-water quality (forested area). The sampling sites Gidra: Píla, Parná: Majdán and Trnávka: Buková are identical with the water gauge of the Slovak Hydrometeorological Institute (SHMI).

The temporal variability of the nitrate nitrogen concentrations was very similar in all 4 stations in the period 1991–1994 (Fig. 4). Therefore we decided to focus on variability of the pollution concentrations only in Parná River at sampling site Horné Orešany water gauge (upstream the small reservoir Horné Orešany) and the sampling program was completed by another sampling site below the water reservoir in Horné Orešany village.

Methods

The statistical analysis of daily discharge series included the testing of homogeneity, stationarity, autocorrelation, multiannual cyclicity and long-term trends in measured data series. For testing we have used the autocorrelation and spectral analysis with application of the AnClim software (Štepánek, 2010).

At the trend analysis of the time series, the parametric and non-parametric tests can be used (Procházka et al., 2001). The parametric test considers the linear regression of the random variable x_i on time. The parameters of the trend line are calculated by using standard method for estimation of the parameters of a simple linear regression model, i.e. by using least square method. To identification of the long-term trends we used Mann-Kendall nonparametric trend test. The Mann-Kendall nonparametric test (M-K test) is one of the most widely used non-parametric tests for significant trends detection in time series. By M-K test, we want to test the null hypothesis H_0 of no trend, i.e. the observations x_i are randomly ordered in time, against the alternative hypothesis H_1, where there is an increasing or decreasing monotonic trend.

The maximum concentrations of nitrates in surface water usually occur during the high discharges period (see Fig. 4) and therefore the impact of discharge cannot be omitted when analysing the mean (monthly, annual) nitrate concentrations. In order to assess the mean nitrate concentrations we have to calculate the weighted mean with respect to discharge, it means to calculate the mean concentration of nitrates in the stream according to the relation (Pekárová et al., 1995; Pekárová and Pekár, 1996):

$$C_q = \frac{\sum_{i=1}^{m} C_i . Q_i}{\sum_{i=1}^{m} Q_i} . \qquad (1)$$

where

C_i – measured nitrate concentrations, [mg l^{-1}];
Q_i – measured discharge, [m^3 s^{-1}];
C_q – weighted mean of nitrate concentrations, [mg l^{-1}];
m – number of measured data.

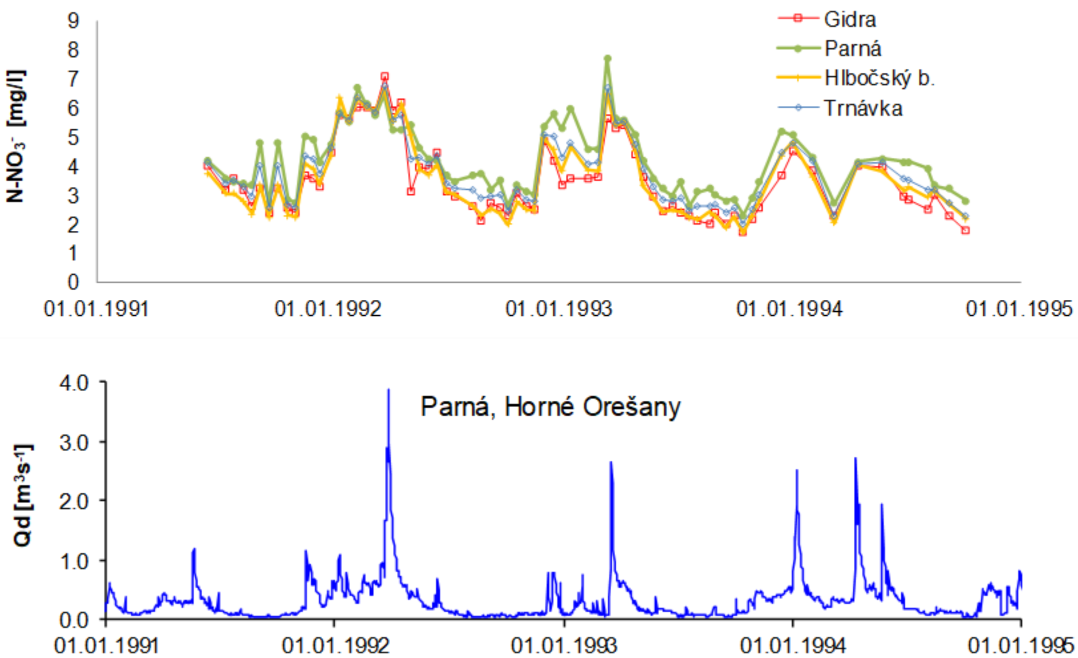


Fig. 4. The temporal variability of observed nitrate nitrogen concentrations in stream water, the Little Carpathians sampling sites, June 1991–October 1994 and daily discharge at Parná River: H. Orešany.

Results

Discharge analysis

The water gauge of Parná: Horné Orešany (Number 5250, river km 26.8) is situated above the water reservoir Horné Orešany (Výleta et al., 2017). The average annual discharge of the Parná River at the station of Horné Orešany for the period of 1961–2018 was 0.351 $m^3 s^{-1}$. The minimum and maximum flow observed during this period was 0.025 $m^3 s^{-1}$ and 7.653 $m^3 s^{-1}$, respectively. Other statistical characteristics can be found in Table 2.
On Fig. 5a, we can observe the variability of dry and humid periods. Periods 1971–1974, 1989–1991, 2001–2003, and 2017–2018 were extremely dry. The regularity of changing the dry and humid years was studied by the autocorrelation and spectral analyses of mean annual discharge time series (Fig. 5b). Autocorrelogram shows significant autocorrelation near the 14^{th} year. This period was proved by the spectral analysis as well. The spectral analysis identified also other multiannual cycles: 4.5–5.5 years; 3.6 years, and 2.4 years. With respect to this more or less regular variability we can expect the more humid years to come.
The intraannual variability of mean, maximum, and minimum daily discharge did not change significantly (Fig. 5c).
On the other hand, the discharges are decreasing from the long-term point of view. With respect to the multi-annual cycles of low and high discharges, we recommend to estimate the long-term trend since low period around year 1971 to low period around year 2018, (see results in the Table 3). Flows decreased slightly during this period, but the trend is not statistically significant.

Nitrate concentrations in surface water

Nitrates are of significant seasonal variability. Higher nitrate values occur during snow-melting in spring (Mendel, Halmová, 1993; Pekárová et al., 1994; Hyánková et al, 1995; Pekárová, Pekár, 1996). Incorrect application of fertilizers during the vegetation period leads to a rapid increase of nitrate concentration in stream waters. The time variation of measured nitrate concentrations is shown in Fig. 4.
In Table 4 there are summarised the estimated means of nitrate nitrogen in three different periods and calculated by two different approaches:

1. Arithmetic average of measured data,
2. Weighted average with respect to discharge according to Eq. (1).

The highest nitrate pollution was found at the Parná River, above Horné Orešany in the first period 1991–1994, where average nitrate concentrations reached 4.2 mg l^{-1}, and weighted average 5.11 mg l^{-1}. After 1993 nitrate concentration in Parná headwater decreased.

Hydrological regime and estimation of nitrate nitrogen concentrations in the stream

As already mentioned, the water quality has a strong seasonal dependency, especially for some matters. Nitrate concentrations reach their maximum values during the wet periods, mainly during the spring snow melting. In Parná River, the minimum concentrations occur in summer-autumn (June–November), while the maximum concentrations are measured between December and May (Fig. 6a). Rain water washes nitrates off from the surface into a river. Generally, in the rivers of the Little Carpathian headwater region, an increased discharge leads to an increase in the nitrate concentration. But, during big floods, the nitrates concentration starts to be diluted by increasing discharge. We have derived exponential empirical relations for estimation of the nitrate nitrogen concentrations in the Parná River stream (Fig. 6b) based on mean daily discharge Q_d during the sampling day.
In period 1991–1994:

$$N\text{-}NO_3^- = 5.5176.Q_d^{0.1984} \quad \text{for } Q_d < 2 \qquad (2)$$

$$N\text{-}NO_3^- = 15.785.\exp(-0.375.Q_d) \quad \text{for } Q_d \leq 2 \qquad (3)$$

In period 2004–2018:

$$N\text{-}NO_3^- = 4.5315.Q_d^{0.4001} \quad \text{for } Q_d < 2 \qquad (4)$$

$$N\text{-}NO_3^- = 15.785.\exp(-0.375.Q_d) \quad \text{for } Q_d \leq 2 \qquad (3)$$

Conclusions

In Slovakia, the application of industrial fertilizers decreased significantly due to decrease of the agricultural mass production 30 years ago after 1989. The decrease in production impacted positively the decrease of nitrogen content in surface waters in Slovakia. After 20 years, since 2010, the fertilization dozes have increased to values close to the original ones before 1989. It can be expected that the nitrate concentrations will increase as well in our streams. Moreover, due to increasing air temperature (global warming) the evaporation increases as well and river runoff is decreasing slowly. The most

Table 2. Basic discharge statistical characteristics of the Parná: H. Orešany River, 1961–2018 period. *Q* – discharge, *q* – specific runoff, *R* – runoff depth

	mean	min	max	330-day	30-day	c_s	c_v
Q [$m^3 s^{-1}$]	0.351	0.025	7.653	0.078	0.810	5.209	1.264
q [$l\ s^{-1} km^{-2}$]	9.284	0.660	202.14	2.060	21.395		
R [mm]	292.8						

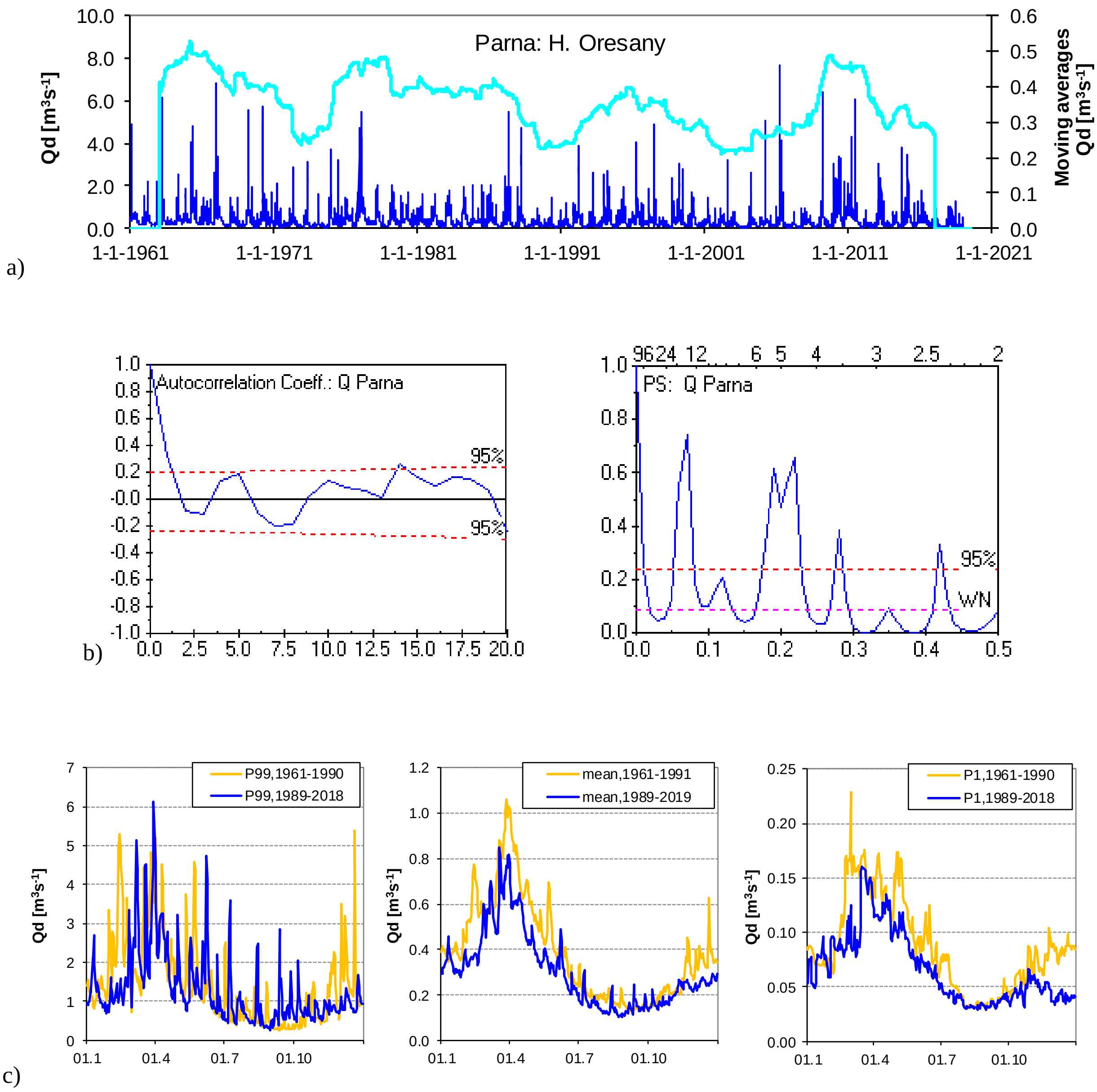


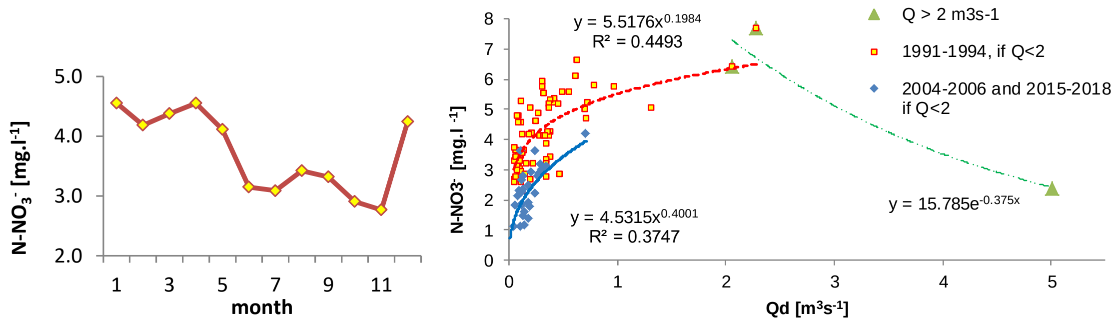
Fig. 5. a) Daily discharge and 4-years moving averages. Parná: H. Orešany; b) Plots of the autocorrelogram and power spectrum (MESA method), annual discharge. c) Long-term daily discharge for two periods, P99 – 99th percentiles, long-term mean daily discharge, and P01 – 1st percentiles.

Table 3. Results of annual discharge M-K trend tests for selected time periods, gauging station Parná: H. Orešany *(– level of significance α=0.01; * – level of significance α=0.05;)***

				Mann-Kendall trend				Sen's slope estimate			
Time series	**First year**	**Last year**	***n***	**Test Z**	**Signific.**	***A***	***A*$_{min\,95}$**	***A*$_{max\,95}$**	***B***	***B*$_{min\,95}$**	***B*$_{max\,95}$**
Qa	1961	2018	58	-2.80	**	-0.0030	-0.0050	-0.0010	0.4351	0.4814	0.3765
Qa	1971	2018	48	-1.38		-0.0020	-0.0046	0.0007	0.3998	0.4736	0.3126
Qa	1961	2011	51	-2.18	*	-0.0030	-0.0053	-0.0003	0.4341	0.4828	0.3692

Table 4. **Basic statistical characteristics of estimated nitrate nitrogen concentrations in Parná stream [mg l^{-1}], at Horné Orešany sampling site, three periods**

River	Parná	Parná	Parná
Period	1991–1994	2004–2006	2015–2018
Average	4.20	2.34	2.30
Weighted average according Eq.(1)	**5.11**	**2.69**	**2.49**
Min	2.27	1.08	1.08
Max	7.70	4.19	3.60
Std. deviation	1.16	0.79	0.81



a *b*

Fig. 6. a) Monthly regime of the nitrate nitrogen concentrations; b) Relationships between N-NO_3^- concentrations and daily discharge, in the Parná River

endangered are the lowland streams in agricultural areas. The aim of this study was to assess the long-term development of the hydrological regime of the Parná River at Horné Orešany gauge during the period 1961–2018 and to assess the development of the nitrate nitrogen concentrations at this sampling site during the period 1991–2018.

The analysis of the hydrological regime proved the changing of wet and humid periods in approximately 14-years cycles in the Parná River series. In the main the discharge is decreasing slightly.

In the case of nitrate nitrogen concentrations the marked decrease occurred in this river basin from the value of 5.11 mg l^{-1} during the years 1991–1995 to the value of 2.49 mg l^{-1} in the years 2015–2018.

It was shown that the nitrate concentrations in surface streams are increasing with increasing discharge in the Little Carpathians headwaters, but there exists a threshold value of discharge when the nitrates concentration starts to be diluted by increasing discharge. The relation between discharge and nitrate concentration was used to derive exponential empirical relations for estimation of the nitrate nitrogen concentrations in the stream (Fig. 6b) based on mean daily discharge during the sampling day. These equations can be used for indirect estimation of nitrate nitrogen concentrations when they were not measured directly.

Acknowledgements:

This work was supported by the project VEGA 2/0004/19.

References

Gálik, M. (1990): The Causes of Undesirable Effects of Anthropogenic Activities on the Quality of Groundwater (In Slovak.) PhD Thesis, SVŠT, Bratislava.

Guliš, G., Wittgruber, J., Dubrovčáková, E. (1994): The Development of Drinking Water Quality Sources on Trnavka River Drainage Area (In Slovak.) Vodní hosp., 2, 5–8.

Hyánková, K., Ženišová, Z., Janský, L., Fendeková, M., Flaková, R. (1995): Influence of Agricultural Activity on the Nitrate Content in Drinking Water Sources in Slovakia. Hrvatske vode, Vol. 3, 12, 293–300.

Lehotský, J., Tóth, P. (1992): Springs in the Low Carpathians: Comparison of Two Classifying Criteria. Ecology (Slovakia), Vol. 11, 2, 167–180.

Mendel, O., Halmová, D. (1993): Analysis of the Runoff and Nitrate Loads in Two Small Microbasins. Proc. Abstracts Biogeomon and Workshop on Integrated Monitoring CzGS, Prague, 202–203.

Molnár, L., Miklánek, P., Mészároš, I. (eds.) (1993): International Environmental Programme for the Danube Basin - National Review of Danube Basins in Slovak Republic. Bratislava, ME SR, 476 pp.

Pavelková, D. (2000): Water Quality Characteristics Monitoring in the Drainage Channels in the East Slovakian Lowland. Acta Hydrologica Slovaca Vol. 1, 1, 197–205.

Pavelková, D., Babinec, K. (2017): Nitrate in House Wells in the Villages of Michalovce and Sobrance District (In Slovak). In XXI. Okresné dni vody. ÚH SAV, Výskumná hydrologická základňa, Východoslovenská vodárenská spoločnosť, a.s. Košice, 77–80.

Pekárová, P., Mendel, O., Koníček, A., Halmová, D. (1994): Analysis of the Selected Pollutants in Forested Catchments in the Carpathian Region. Proc. Developments in Hydrology of Mountainous Areas, Stará Lesná, 97–98.

Pekárová, P., Miklánek, P., Rončák, P. (1995): Stream Load and Specific Yield of Nitrogen and Phosphates from Slovakia. J. Hydrol. Hydromech., Vol. 43, 4–5, 233–248.

Pekárová, P., Miklánek, P. (2013): Surface and Ground Water Pollution by Nitrates in Eastern Slovakia. The 13th International Multidisciplinary Scientific GeoConference SGEM 2013: Hydrology and Water Resources, Soil, Forest Ecosystems, Marine and Ocean Ecosystems, Sofia: STEF 92, 341–348.

Pekárová, P., Onderka, M. (2005): Nitrate Concentration Modeling in Vydrica Stream by an Empirical Model. Acta Hydrologica Slovaca, Vol. 6, 1, 141–148.

Pekárová, P., Pekár, J. (1996): The Impact of Land Use on Stream Water Quality in Slovakia, Journal of Hydrology, Vol. 180, 333–350.

Pekárová, P., Pekár, J. (1998): The Chemical Regime and Interaction of Surface and Groundwater in Small Carpathian Region, Ekologia-Bratislava, Vol. 17, 4, 391–401.

Pekárová, P., Sebíň, M., Pekár, J., Onderka, M., Miklánek., P. (2008): Simulation of the Impact of Fertilizer Dozes on Nitrate Concentrations in the Stream. Cereal Research Communications, ISSN 0133-3720, Vol. 36, 1051–1054.

Pekárová, P., Velísková, Y. (1998): Water Quality Modeling in the Ondava Catchment Area, VEDA, Bratislava, 256 p.

Procházka, M, Deyl, M, Novický, O. (2001): Technology for Detecting Trends and Changes in Time Series of Hydrological and Meteorological Variables - Change and Trend Problem Analysis (CTPA). User's Guide. CHMI, Prague; 25 p.

Sebíň, P., Pekárová, P., Miklánek, P. (2007): Nitrate Wash Off from the Bratislava Forest Park Basin Vydrica in Years 1986–2005, J. Hydrol. Hydromech., Vol. 55, 3, 145–155.

Slaninka, I., Dlapa, P., Kordik, J. (2005): Cycle of Selected Substances in Natural Waters of Forest Ecosystem in Upper Vydrica Brook. (In Slovak.) In: Hydrologie maleho povodi, Institute of Hydrodynamics AS CR, Praha, 261–268.

Štěpánek, P. (2010): AnClim – software for time series analysis. Department of Geography, Faculty of Natural Science, MU, Brno. [on-line.] Accessible on www: http://www.climahom.eu/software-solution/anclim

Velísková, Y., Sokáč, M., Halaj, P. (2012): Simulation of Pollution Transport at Upper Part of Ondava River (In Slovak). In Proc. XVI. Okresné dni vody, Michalovce, ÚH SAV, 93–96.

Výleta R., Škrinár A., Danáčová M., Valent P. (2017): Optimizing use of water management systems during changes of hydrological conditions. IOP Conf. Series: Materials Science and Engineering, vol. 245, 10 pp.

WB (2020): http://data.worldbank.org/indicator/AG.CON.FERT.ZS/countries?order=wbapi_data_value_2007%20wbapi_data_value&sort=desc&display=default.

WFD (2000): Directive 2000/60/EC of the European Parliament and of the Council of the 23 October 2000, establishing a framework for Community action in the field of water policy, EU.

RNDr. Pavla Pekárová, DrSc. (*corresponding author, e-mail: pekarova@uh.savba.sk)
RNDr. Pavol Miklánek, CSc.
Institute of Hydrology SAS
Dúbravská cesta č. 9
841 04 Bratislava
Slovak Republic

Doc. RNDr. Ján Pekár, CSc.
Comenius University in Bratislava
Faculty of Mathematics, Physics, and Informatics
Department of Applied Mathematics and Statistics
Mlynská dolina
842 48 Bratislava
Slovak Republic

Ing. Zuzana Danáčová, PhD.
Slovak Hydrometeorological Institute
Jeséniova 17
833 15 Bratislava
Slovak Republic