Time and place changes concentration of nitrite nitrogen in the southwestern part of the Slovak Republic

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Concentrations of nitrite nitrogen in the water flow Čaradice brook were evaluated in the years 2005–2010. Čaradice brook springs in the mountains of Pohronský Inovec in the southern foot of Drienka hill and it is the right tributary of the Hron River, into which mouth near the village Kozárovce. Its length is 11.1 km. Samples of the water in longitudinal profile of the watercourse were carried out from six sampling sites, on a regular basis, in the second decade of the month. The places of taking samples were localized to include all real sources causing the pollution of watercourse. The average concentration of nitrite nitrogen during the whole period represented a value of 0.05 mg dm⁻³. Its share in total inorganic forms of nitrogen (N-NO₃⁻, N-NH₄⁺, N-NO₂⁻) represented 1.98%. Depending on the time of sampling the lowest average concentration for the whole period was recorded in February (0.032 mg dm⁻³). Its highest average concentration was detected in May (0.065 mg dm⁻³). Seasonal dynamics regularity of concentrations of nitrite nitrogen during the whole monitored period is not reflected. Effect of sampling sites on the nitrite nitrogen concentration in the water flow was as significant as the influence of the month. In the longitudinal profile of the watercourse, we generally observed a tendency of gradual increase in the concentration from the first to the last sampling site. The lowest average concentration of nitrite nitrogen (0.025 mg dm⁻³) was found in the sampling site, which was located under the forest ecosystem and the highest (0.066 mg dm⁻³) in the sampling point located below the village Kozárovce. The most significant increase in the average concentration was found in the sampling site located under Čaradice municipalities and Kozárovce, which may indicate contamination of sewage water flow. In the regulation of the Government of the Slovak Republic No. 269/2010 Coll. the recommended value for nitrite nitrogen is 0.02 mg dm⁻³. Calculated values of 90th percentile (P90) of this indicator in all sampling sites were lower than the recommended value of government regulations.

Keywords: nitrite nitrogen, water flow, water quality

1 Introduction
Nitrites are found in all types of waters, however, in lower concentrations than nitrates and ammonia (Barančíková et al., 2009). They are originated by biochemical oxidation of ammonium nitrogen or by chemical reduction of nitrate nitrogen. In surface waters they are found only in very low concentrations, because they are chemically very unstable and usually only accompany nitrate and ammonium nitrogen (Buday, 2002; Aber, 2002). Most of the nitrites are very well soluble in water. In natural waters, nitrites never dominate between the organic forms of nitrogen because in oxic conditions they are quickly transformed into nitrates. In the inorganic form they are present in rainfall water. Higher concentrations of nitrites are found in sewage effluent water and in some waste waters from machine engineering factories. In surface waters they are undesirable, since they have a toxic effect on water ecosystem (Lichvárová et al., 2006). The aim of the paper was to evaluate concentrations of nitrite nitrogen in the water flow Čaradice brook were evaluated in the years 2005–2010.

2 Material and methods
Čaradice brook springs in the mountains of Pohronský Inovec in the southern foot of the hill Drienka (751.1 m) at an altitude of about 600 above sea level. The brook flows through the territories of Zlaté Moravce and Levice districts. It a right tributary of the river Hron, its length is 11.1 km. Near the village of Kozárovce a uniform reservoir called „Dam“ was built, which is located between the villages Čaradice and Kozárovce. It is used for irrigation and sports fishing. From the right side, from the area of Sejovský hill (295.2 m above the sea level) flows the largest tributary of Čaradice brook – the Saint brook, from the left side it has only short tributaries. The flow direction is predominantly north-south, on the lower reaches northeast. Čaradice creek flows into the river

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Hron near the village Kozárovce, in the area called Slovak gates, at an altitude of about 174 above sea level in relation to hydrographic conditions. Čaradice stream flows in the uplands – lowland area which is characterized by the type of rain snow runoff with the highest flow rate in March and lowest in the month of September. According to the geological characteristics of the soil it has been shaped over the several stages of volcanic activity with rotation periods of destruction and denudation of volcanic complexes. Andesine, rhyolite and basalt neovolcanites are interspersed there (Konečný, 1998). The territory belongs to the warm area and slightly dry subarea. The average temperature in 2005 was 9.1 °C, in 2006 – 9.7 °C, in 2007 – 8.9 °C, in 2008 – 9.4 °C, in 2009 – 9.8 °C and in 2010 – 10.03 °C. The average rainfall in 2005 represented 711.4 mm, in 2006 – 842.7 mm, in 2007 – 569.8 mm, in 2008 – 679.7 mm, 2009 – 684.4 mm and 687.7 mm in 2010 (source: Kozárovce precipitation measuring stations). In the upper segment of the river basin watercourse forest ecosystems and permanent grassland are situated. The greater part of the stream flows through the agroecosystem of agricultural crops on the arable land. In terms of agro-productions the territory ranks to the corn – sugar beet region. Plant production is focused mainly on cereals growing (wheat, winter rye, and spring barley, maize for grain and for silage), perennial forage crops (Lucerne) and oilseeds (rapeseed, sunflower). Livestock production is oriented on the cattle breeding. Farmed land near the watercourse belongs to the cadaster of the agricultural cooperative of Volkovce (source: Volkovce Agricultural Cooperative).

Samples of the water from Čaradice brook were carried out on a regular basis, in the second decade of the month in the years 2005–2010. The places of taking samples were localized in a longitudinal profile of the watercourse to include all sources causing the changes of dissolved oxygen concentration. Samples of water were collected from six sampling sites. Water samples were taken from the middle of the main stream.

- 1st sampling site – the forest ecosystem Pohronský Inovec, 48˚ 22’ 56” north latitude and 18˚ 29’ 7.3” east longitude.
- 2nd sampling site – in the north point of Čaradice, 48˚ 21’ 9.1” north latitude and 18˚ 30’ 53” east longitude.
- 3rd sampling site – in the south point of Čaradice, 48˚ 21’ 35” north latitude and 18˚ 30’ 55” east longitude.
- 4th sampling site – before the water tank, 48˚ 19’ 8.2” north latitude and 18˚ 30’ 50” east longitude.
- 5th sampling site – behind the water reservoir in the north point of Kozárovce, 48˚ 19’ 7.4” north latitude and 18˚ 30’ 50” east longitude.
- 6th sampling site – in the south point of Kozárovce, 48˚ 18’ 7.7” north latitude and 18˚ 32’ 25” east longitude.

In the collected water samples were determined nitrite nitrogen – by spectrophotometrically using sulphanilic acid and 1-naphthylamine, which method analogous to DIN 38402 Part 51st. Values of N-NO₂ have expressed in mg dm⁻³.

To the evaluation of the quality of surface water in the sampling sites under the indicator N-NO₂ we used the values of the 90th percentile (P90) was calculated from the measured values and then compared with their matching set of limit values referred to the Regulation of the Government of the Slovak Republic No. 269/2010 Coll.

3 Results and discussion

A quantitatively least represented form of inorganic nitrogen in the water flow was nitrite nitrogen. Its share of total content of inorganic forms of nitrogen (N-NO₃, N-NH₄, N-NO₂) represented 1.98% (Fig. 1). The average concentration of N-NO₂ during the whole reference period was 0.05 mg dm⁻³ (Fig. 2).

The lowest average concentration (0.012 mg dm⁻³) of inorganic nitrogen in the basin of Rybáriky also found Sebiň (2007) and Valent et al. (2011). Lower concentrations of N-NO₂ can be connected with the fact that nitrates are chemically and biochemically labile and oxic conditions they are rapidly transformed into nitrates by nitrification (Noskovič et al., 2010; Aber, 2002).

Depending on the time of collection, the lowest average concentration of N-NO₂ for the whole reference period was 0.05 mg dm⁻³.
of nitrite nitrogen in waters can be recorded after an intensive rainfall activity.

Babošová, Noskovič (2014) indicate that average rainfall nitrite nitrogen inputs to land on an experimental basis Malanta (Nitra) in the years 2005–2006 were 0.05 kg ha⁻¹. The seasonal regularity of N-NO₂⁻ dynamics concentration during the whole reference period was not demonstrated. The concentration of nitrite nitrogen was also significantly influenced by the sampling place. The lowest average concentration of nitrite nitrogen (0.025 mg dm⁻³) was found in the sampling place no. 1 (under the forest ecosystem) and the highest (0.066 mg dm⁻³) in the sampling place no. 6 (under the village of Kozárovce) (Fig. 4). The most significant increase of nitrite nitrogen average concentration was found in the sampling places located under the villages of Čaradice and Kozárovce, which may indicate contamination of the flow due to sewage wastewaters.

From the one-dimensional test of significance for the N-NO₂⁻ concentration it follows that changes in values were significantly influenced by the year, month and sampling place (Table 1).

In the regulation of the Government of the Slovak Republic No. 269/2010 Coll. The recommended value for nitrite nitrogen is 0.02 mg dm⁻³. Calculated values of 90th percentile (P90) of this indicator in all sampling sites were lower than the recommended value of government regulations.

Table 1  Analysis of variance for concentrations of N-NO₂⁻

| Effect           | Sum of squares | Degrees of freedom | Mean square | Value F | Evidence supporting |
|------------------|----------------|--------------------|-------------|---------|---------------------|
| Absolute term    | 0.802941       | 1                  | 0.802941    | 1987.04 | 0.000000            |
| Year             | 0.008571       | 5                  | 0.001714    | 4.252   | 0.000903            |
| Month            | 0.016983       | 11                 | 0.001544    | 3.821   | 0.000030            |
| Sampling site    | 0.077362       | 5                  | 0.015472    | 38.289  | 0.000000            |
| Error            | 0.163252       | 404                | 0.000404    |         |                     |
4 Conclusions
In the water of Čaradice brook which springs in the mountains of Pohrons ký Inovec located in the southwestern part of the Slovak Republic, the nitrite nitrogen concentration was evaluated during 2005–2010. Average nitrite nitrogen concentration across the whole evaluated period represented value of 0.05 mg dm⁻³. Depending on the time of collection, the nitrite nitrogen lowest average concentration for the whole reference period was recorded in February (0.032 mg dm⁻³) and the highest concentration was in May (0.065 mg dm⁻³). The most significant increase of nitrite nitrogen concentration was recorded in the year 2009 during September. The seasonal regularity of N-NO₂ dynamics concentration during the whole reference period was not demonstrated. Depending on the place of sampling, the lowest average concentration of nitrite nitrogen (0.025 mg dm⁻³) was found in the sampling place, which was located under the forest ecosystem and the highest (0.066 mg dm⁻³) in the sampling place being located under the village of Kozárovce. The most significant increase of its average concentration was found in the sampling place located under the villages of Čaradice and Kozárovce, which may indicate contamination of the flow due to sewage wastewaters. Base on the calculated values of 90-th percentile (P90) of this indicator we found that in all sampling sites were lower values than the recommended value of government regulations.

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References
ABER, J.D. et al. (2002) Is Nitrogen Deposition Altering the Nitrogen Status of Northeastern Forests. American Geophysical Union, vol. 31, 6 pp.
BABOŠOVÁ, M. and NOSKOVIČ, J. (2014) The quality of atmospheric precipitation in the area of Nitra – Lower Malanta. Nitra: Slovak University of Agriculture in Nitra. 64 p.
BARANČÍKOVÁ, G. et al. (2009) Environmental Chemistry. Prešov: Prešov University. 251 p.
BUDAY, J. (2002) Intensification of the process of removing nitrogen from sewage – substrate and product inhibition of nitrification. Bratislava, pp. 92.
KABELKOVÁ-JANČÁRKOVÁ, I. (2002) Nitrification dynamics in a small watercourse. Water management, vol. 52, no. 8, pp. 221–224.
KONEČNÝ, V. (1998) Geological map of the Štiavnické hills and Pohrons ký Inovec. VEDA: Bratislava.
LICHVÁROVÁ, M. et al. (2006) Properties of water. Project KEGA 3/3004/05.
GOVERNMENT DECREE of the Slovak Republic No. 269/2010 Coll.
NOSKOVIČ, J. et al. (2010) Zitavsky luh – abiotic components. Nitra: Slovak University of Agriculture in Nitra. 157 p.
NOSKOVIČ, J. et al. (2011) Nature Reserve Alúvium Žitava water quality. Nitra: Slovak University of Agriculture in Nitra. 105 p.
PITTER, P. (1999) Hydrochemie. Prague, pp. 568.
PITTER, P. (2009) Hydrochemie. 4th ed. Prague, pp. 568.
SEBIŇ, M., PEKÁROVÁ, P. and MIKLÁNEK, P. (2007) Evaluation and indirect estimation of nitrate losses from the agricultural microbasin Rybárik. Biologia, vol. 62, no. 5, pp. 569–572.
VALENT, P. et al. (2011) Analysis of nitrate concentrations using nonlinear time series models. Journal of Hydrology and Hydrochemics, vol. 59, no. 3, pp. 157–170. doi: http://dx.doi.org/10.2478/v10098-011-0013-9