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Concentration of nitrate and ammonium nitrogen in different ecosystems

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Abstract

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This work investigates the effect of forest, agricultural and human settlement ecosystems on the concentrations of N-NO_3^-, N-NH_4^+ in the water course Čaradický potok stream based on the data assembled between 2005–2010. The water flow has its springs in the Pohronský Inovec Mts, and then it crosses the districts Zlaté Moravce and Levice. Analysing the results obtained we can see that the lowest average concentrations of the monitored inorganic nitrogen forms within the whole study period were recorded in a sampling site situated under forest ecosystems of Pohronský Inovec. The average concentration of N-NO_3^- in the water Čaradice brook was 2.26 mg dm^{-3}. The highest average concentration for the whole monitoring period was observed in January, the lowest in August. The most remarkable increase in the concentrations of N-NO_3^- was found in September 2009, probably related to an intense rainfall before the sampling (20.5 mm on 29th September 2009). Among the sampling sites, the maximum average concentration of N-NO_3^- was measured in the sites located in ecosystems under direct influence of human settlements (the villages of Kozárovce and Čaradice). These high values were probably due to a secondary increase in nitrate nitrogen resulting from nitrification of ammonium nitrogen supplied with contaminated sewage effluents (no sewage tanks in these villages). The increase in the average concentration of N-NO_3^- in the studied water course was during the entire study period caused both by an permanent grassland agroecosystem (sampling site No. 2) and an arable land agro-ecosystem (sampling site No. 4) located in the water catchment basin. The asset of these agro-ecosystems, however, was lower than the one of the urban ecosystems. By variance analysis, were detected three statistically significant factors (year, season and site) affecting the concentration of nitrate nitrogen. The average concentration of amonium nitrogen during the whole monitoring period represented 0.20 mg dm^{-3}. The lowest concentrations were recorded in winter and the highest in summer. The minimum average concentration was measured in February, the maximum in July. Depending on the sampling site, the highest average concentration values throughout the whole monitoring period were obtained in the sampling sites under human settlements (villages of Kozárovce and Čaradice). The variance analysis for N-NH_4^+ revealed a statistically highly significant effects of sampling date (month) and site.

Key words

amonium nitrogen, nitrate nitrogen, water stream

Introduction

Nitrogen occuring in water in various forms is subject to a variety of macrobiological, chemical and physical processes (Bublinec, 1991; Bublinec et al., 1994). It belongs among the most important microbiogenic elements (Bublinec, 1992; Hruška et al., 2006) and the main nutrients limiting and supporting eutrophication processes of surface waters (Šileika et al., 2005). According to Pitter (2009), inorganically bound nitrogen is important summary indicator of contaminating sewage and surface water. Darrecq et al. (2008) and (Hruška, 2006) consider the following main sources of nitrogen: uncleaned sewage water, agricultural activities (incorrect application of fertilizers and unsuitable agro-technical measures) near water courses and contaminated precipitation. Nitrates are present in small concentrations in almost all surface waters (Stoddard, 2004; Campell, 2000). Ammonium nitrogen is a primary product of decomposition of organic nitrogenous substances of animal and plant origin (Buday, 2002). In waters at oxygen presence, is ammonium nitrogen unstable and easily susceptible to biochemical oxidation (nitrification) (Pitter, 2009).

Material and methods

Research area

The Čaradický brook has its springs in the Pohronský Inovec Mts, in the southern foothill of the mount Drienka (751.1 m a.s.l.) at about 600 m a.s.l. The studied brook Čaradický potok is a right tributary of the Hron river. It is long 11.1 km, and flows across the districts of Zlaté Moravce and Levice. The upper stream is flowing on the bottom of the Certova valley ended with an area with a holiday resort Calex, a hamlet named Široký prieloh and a castle. Above the village of Kozárovce, between the villages Čaradice and Kozárovce, there was built a uniform-shaped water reservoir – dam. The largest tributary of the Čaradický potok is the Svätý potok stream, flowing from the right side of the mount Sejovský (295.2 a.s.l.) On the left side, there are only short tributaries. The flow direction is predominantly north-south, being south-east in the downstream. The Čaradice brook is mouthing into the Hron river, in the so-called Slovakian gate 174 m above sea level, near the village of Kozárovce.

According to characteristics of the geological subsoil, the region is an interesting vast and old volcanic-type structure, which was formed by changing of several phases of volcanic activity and periods of destruction and denudation of volcanic complexes. Andesite, rhyolite rocks and Basalt neovolcanites are alternated in the locality. Beside the rocks of volcanic origin, nappe limestones can also be found (Konečný, 1998).

The studied area belongs to a warm and slightly dry sub-region. The average temperature was 9.1 °C in 2005, 9.7 °C in 2006, 8.9 °C in 2007, 9.4 °C in 2008 and 9.8 °C in 2009. The average rainfall represented 711.4 mm in 2005, 842.7 mm in 2006, 569.8 mm in 2007, 679.7 mm in 2008, and 684.4 mm in 2009 and 690.5 mm in 2010 (source: The rainfall measuring station Kozárovce).

The upper part of the water shed is covered with forest ecosystems and permanent grasslands. The major part of the water course passes through agro-ecosystems of agricultural crops on arable land. The dominant soil types in the area of interest are: brown soils; chernozem, brown soil; chernozem calcareous soil; chernozem and gley fluvial soil.

From an agricultural and industrial point of view, this territory is included in the corn- beet farming region. The crop production is mainly focused on cultivation of cereals (winter wheat, winter rye, spring barley, maize grain, maize silage), perennial forage (medicinal) and oilseeds (rape, sunflower). The livestock production is focused on cattle breeding. The cultivated land in the vicinity of the watercourse belongs to the Agricultural profit-sharing co-operative farm Volkovce.

Concerning industrial fertilizeres, in the course of the monitoring period was applied urea in a dose of (N = 46%), DAM 390 (N = 30%), NPK 15:15:15 at 200 kg ha^{-1} (N = 12%, P_2O_5 = 19%, K_2O = 19%), LAV at a dose of 350 kg ha^{-1} (N = 27%), DASA at 250 kg ha^{-1} (N = 26%, S = 13%). Nitrogen fertilizers were applied at an average dose of 138 kg ha^{-1} year^{-1}, phosphatic fertilizers at 39 kg ha^{-1} year^{-1} and potassium at 6.01 kg ha^{-1} year^{-1}. In the autumn of 2008 was applied ground limestone at a dose of 2 t ha^{-1}. As for the organic fertilizers, farmyard manure was applied in the root–crops in a dose of 40 t ha^{-1} year^{-1} (source: Co-operative farm Volkovce).

Sampling and processing of the material

Water samples were collected from 6 sampling sites along the water stream Čaradický brook, in the second decades of all calendar months in the years 2005–2010. The sampling sites were located in such a way as to comprise all the actual watercourse contamination.

Sampling site 1 – under the forest ecosystems Pohronský Inovec, 48˚ 22‘ 56“ N and 18˚29‘ 73“ E.
Sampling site 2 – above the village Čaradice, 48˚21‘91“ N and 18˚30‘53“ L.
Sampling site 3 – under the village Čaradice, 48˚21‘35“ N and 18˚30‘55“ E.
Sampling site 4 – in front of the water tank, 48˚19‘82“ N and 18˚30‘50“ E.
Sampling site 5 – the water tank above the village Kozárovce, 48˚19‘74“ N and 18˚ 30‘ 50“ E.
Sampling site 6 – the village Kozárovce, 48˚ 18‘ 77“ N and 18˚32‘25“ E.

In the collected water samples were determined concentration values of nitrate nitrogen $N\text{-}NO_3^-$ (spectrophotometrically, using WTW nitrospectral in concentrated sulphuric acid, the method is analogous to DIN 38402 Part 51) and ammonium nitrogen $N\text{-}NH_4^+$ (spectrophotometric indophenol blue – Bertholot reaction method is analogous to DIN 38402 Part 51).

For evaluation of surface water quality indicators in terms of $N\text{-}NO_3^-$ and $N\text{-}NH_4^+$ content is used the 90th percentile (P90) quantile calculated from the measured values and the subsequent comparison with the corresponding system of limit values given by the Government Decree of the Slovak Republic No. 269/2010 Coll.

The statistical evaluation was carried out with using the SAS statistical system. For the monitored variables were calculated their basic statistical characteristics of individual sets of values (Table 1). Analysis of variance was performed for three qualitative factors (year of collection, month of collection and sampling site) (Table 2).

Table 1. Basic statistic charakteristic of selected indicators

Indicator	$N\text{-}NO_3^-$	$N\text{-}NH_4^+$
Unit	mg dm^{-3}	mg dm^{-3}
Number	426	426
Mean	2	0.18
Minimum	9.3	1.27
Maximum	0.1	0.01
Std. deviation	1.2786175	0.1356676

Results and discussion

From the studied forms of inorganic nitrogen ($N\text{-}NO_3^-$, $N\text{-}NH_4^+$) in the water course, the most abundant was nitrate nitrogen. Its mean concentration ranged from 2.00 (2008) to 2.97 mg dm^{-3} (2010). For the entire monitoring period, it represented 2.26 mg dm^{-3} (Fig. 1). Lower average concentrations of $N\text{-}NO_3^-$ (1.0 mg dm^{-3}) were recorded by Krúpová in the upper part of the Hron river (2009); and by Bublinec and Dubová (1998a, 1998b) in surface water in the net of the Danube distributaries (1.9 mg dm^{-3}). Another signicantly lower average concentration of $N\text{-}NO_3^-$ (0.4 mg.dm^{-3}) was recorded by Bublinec and Gregor (2002) in the forest ecosystems. On the contrary, higher average concentrations were detected by McIssac and Libra (2003) in the water course Moines (6.3 mg dm^{-3}), Hruška et al. (2006) in the water course Blue brook (3.8 mg dm^{-3}) and Šileika et al. (2010) in water courses Graisupis brook (4.6 mg dm^{-3}), Vardas brook (3.6 mg dm^{-3}) and Lyzina brook (3.1 mg dm^{-3}).

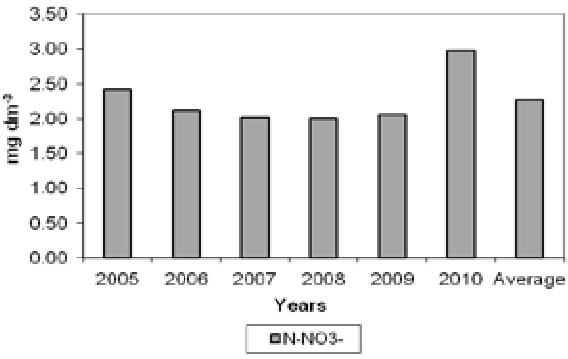

Fig. 1. Mean $N\text{-}NO_3^-$ concentrations in years 2005–2010 [mg dm^{-3}].

Depending on the sampling date, the highest average concentration for the whole period was recorded in the winter, and the lowest in the summer and the autumn season. The maximum average concentration was found in January (3.13 mg dm^{-3}) and the minimum in August (1.61 mg dm^{-3}) (Fig. 2). An analogous seasonal dynamics of these concentrations was recorded by Noskovič et al. (2008) in the water course Čabajský stream, and by Sebíň (2007) in the water stream Lesný. According to Sullivan et al. (2005) concentrations of $N\text{-}NO_3^-$ in surface waters in the summer period decline because they are pumped by phytoplankton. Molénat et al. (2002) suggest a hypothesis that higher concentrations of $N\text{-}NO_3^-$ occur in winter months and their decrease in the summer months is influenced by hydraulic pressure of groundwater level the level of which in soil is higher than is the water level in the water body. Thus, the soil water reaches the layers rich in $N\text{-}NO_3^-$, it enters watercourse with underground waters and, in such a way, acts as an important factor increasing

Table 2. Anova – Analysis of variance for $N\text{-}NO_3^-$ and $N\text{-}NH_4^+$

Source	Dependent variable	Type III Sum of squares	Df	Mean square	F	Sig.
Year	$N\text{-}NO_3^-$	48.06270	5	9.61255296	9.784819	9.01E-09
	$N\text{-}NH_4^+$	0.26601	5	0.05320279	3.308602	0.006201
Month	$N\text{-}NO_3^-$	144.29200	11	13.11750990	13.352590	2.38E-21
	$N\text{-}NH_4^+$	0.57746	11	0.05249721	3.264724	0.000285
Site	$N\text{-}NO_3^-$	90.29550	5	18.05910890	13.212750	6.67E-12
	$N\text{-}NH_4^+$	0.56442	5	0.11288569	6.619619	6.25E-06
Error	$N\text{-}NO_3^-$	347.76700	354	0.98239453		
	$N\text{-}NH_4^+$	5.69237	354	0.01608014		
Total	$N\text{-}NO_3^-$	2942.84000	426			
	$N\text{-}NH_4^+$	25.68	426			

the content of nitrate nitrogen in surface waters. On the contrary, when the ground water level begins to decline in the late spring, leaching of nitrogen from these layers rich in N-NO_3^- shows a decline too, which then results in a decrease in its content in the water course. The most significant increase in concentration of N-NO_3^-, depending on the sampling date was found in 2009 in September. Compared with August, the concentration was higher by 2.12 mg dm^{-3} (i.e. by 34.16%). We assume that this increase in concentration of N-NO_3^- was related to an intensive rainfall event before collecting the water samples (20.5 mm on 29 September 2009). The heavy rain flushed the surface soil layers away, and thus the nitrate nitrogen entered the watercourse. In addition, several authors declare that atmospheric precipitation is an important source of nitrogen (Bublinec and Dubová, 1993; Noskovič and Gábriš, 1995; Bublinec and Dubová, 1998c; Noskovič et al., 2000; Bublinec et al., 2002; Babošová et al. 2007; Pitter, 2009). There have not been recognised any regular seasonal patterns of the dynamics of N-NO_3^- concentration for the whole period of observations.

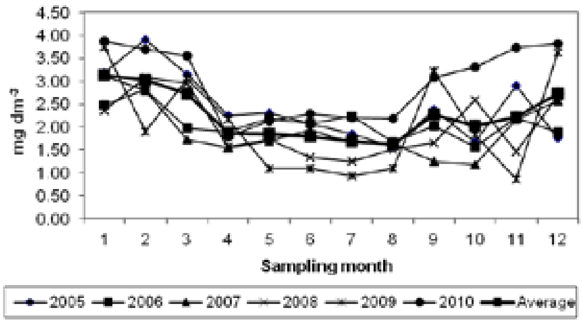

Fig. 2. Mean N-NO_3^- concentrations depending on sampling time [mg dm^{-3}].

Along the entire water course, the minimum average concentration of nitrate nitrogen for the whole period was recorded in the sampling site No. 1 (1.68 mg dm^{-3}), which was located under the forest ecosystem of the Pohronský Inovec Mts (Fig. 3). By analogy, the lowest average concentration of N-NO_3^- in the water course Hontiansky potok was detected by Noskovič (1999) in forest ecosystems. The maximum average concentration for the entire monitoring period was obtained in the sampling site No. 6 (under the village Kozárovce). In the above sampling site, as well as in the sampling site No. 3 (village Čaradice), were detected the most significant increases throughout the study period. Increases in these concentrations in the given ecosystems human settlements were probably caused by a secondary increase in nitrate nitrogen content, due to nitrification of ammonium nitrogen contained in the contaminated sewage water effluents (the village have no sewage tanks). The increase in the average concentration of N-NO_3^- in water course over the entire study period was mainly affected by the the agro-ecosystem of permanent grassland (sampling site No. 2) and arable land agro-ecosystem (sampling site No. 4) located in the water course-basin. The decrease under the agro-ecosystems observed was, however, lower compared to the human settlement ecosystem. Along the water course, under the water basin was observed a decrease in the average concentration of N-NO_3^- for the whole period. This decrease may be caused by a lower concentration of oxygen in the water basin, which probably reduced nitrification. With variance analysis (Table 2) applied for individual factors it was found out that all these three factors (year, month and place of collection) affected statistically significantly the concentration of nitrate nitrogen in water. According to the Government Decree of the Slovak Republic No. 269/2010 Coll., there is given a limit value for nitrate nitrogen making 5 mg dm^{-3}. The obtained 90 percentile values of this indicator were lower than the value recommended.

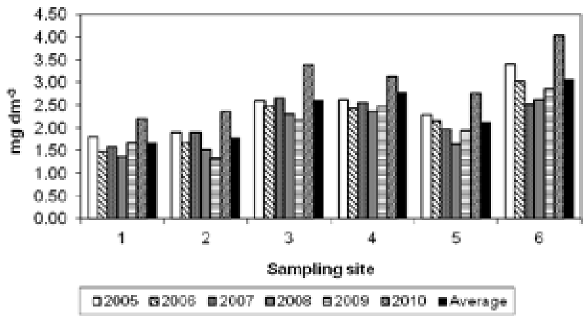

Fig. 3. Mean N-NO_3^- concentrations depending on sampling site [mg dm^{-3}].

The average concentrations of ammonium nitrogen in the studied years were within the range 0.17 (2007) –0.24 mg dm^{-3} (2005). For the whole period, the average concentration of this nitrogen form was 0.21 mg dm^{-3} (Fig. 4). A lower average concentration of N-$NH4^+$ (0.14 mg dm^{-3}) was recorded by Menyhártová (2010) in the Hraničný potok stream, while the highest values were obtained by Sullivan et al. (2005) in the water streams Loch brook (0.50 mg dm^{-3}) and Anrews brook (0.90 mg dm^{-3}). A lower average concentration of N-$NH4^+$ (0.15 mg dm^{-3}) was recorded by Bublinec and Gregor (2002) in the Biosphere Reserve Poľana Mts and by Menyhártová (2010) in the Hraničný potok (0.14 mg dm^{-3}). Another significantly lower average concentration of N-$NH4^+$ (0.02 mg dm^{-3}) was recorded by Bublinec et al. (2007) in water sampled from springs of the Biosphere Reserve Poľana, while the highest values were recorded by Sullivan et al. (2005) for the brooks Loch (0.50 mg dm^{-3}) and Anrews (0.90 mg dm^{-3}). The concentration of N-$NH4^+$ was significantly affected by the collection date, and this was confirmed statistically. Lower average concentrations for the whole monitoring period were recorded in the winter season, and higher in the summer season. The minimum was recorded in February (0.14 mg dm^{-3}) and maximum in July (0.28 mg dm^{-3}) (Fig. 5). Increases in the concentration of ammonium nitrogen in the summer monts were also observed by Beňačková and Noskovič (2004); Babošová and Noskovič (2007); Noskovič et al. (2008). This increase in concentration is probably related to higher water temperature and lower oxygen content, which does not provide favorable conditions for nitrification of ammonium nitrogen to nitrate and nitrite nitrogen (Babošová, 2005; Noskovič et al., 2010). The relationship between the average concentrations of both forms of inorganic nitrogen ($N\text{-}NO_3^-$, $N\text{-}NH_4^+$) in individual sampling months is fitted with a declining line, expressing their negative correlation (–0.92) (Fig. 6). The value of reliability ($R^2 = 0.848$) points to a close correlation between the concentrations of these two inorganic forms of nitrogen. Despite this, the concentration of nitrate nitrogen was always higher than the concentration of ammonium nitrogen. There has not been manifested seasonal regularity of the dynamics $N\text{-}NH_4^+$ concentration within the whole study period.

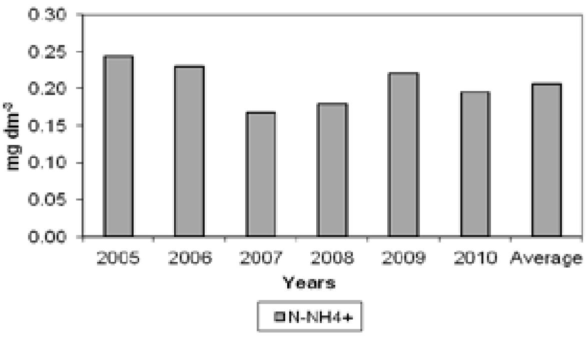

Fig. 4. Mean $N\text{-}NH_4^+$ concentrations in years 2005–2010.

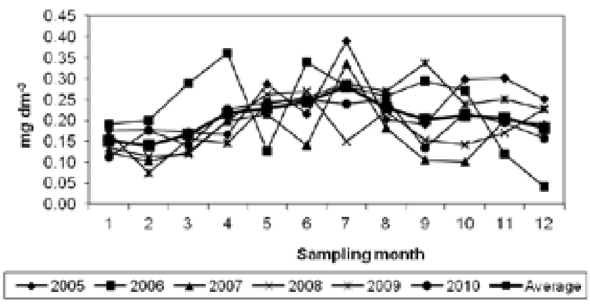

Fig. 5. Mean $N\text{-}NH_4^+$ concentrations depending on sampling time [mg dm^{-3}].

The average concentration of ammonium nitrogen along the watercourse was produced by human settlement ecosystems the water course is flowing through (Fig. 7) and in the water basin. The most significant increase in $N\text{-}NH_4^+$ concentrations depending on the sampling site was detected for the sampling site No. 3 (under the village Čaradice). Compared to the sampling site No. 2 (above the village Čaradice), its $N\text{-}NH_4^+$ concentration was higher by 0.07 mg dm^{-3} (73.07 %), probably due to uncleaned sewage effluents entering the watercourse (Virtanen, 2001; Noskovič, 1992). The analysis of variance (Table 2) for $N\text{-}NH_4^+$ revealed statistically significant effects of qualitative factors, such as month and sampling site. The 90th percentile values declared by the Government Decree of the Slovak Republic No. 269/2010 Coll. are lower than the environmental limit value set for ammonium nitrogen (1.0 mg dm^{-3}).

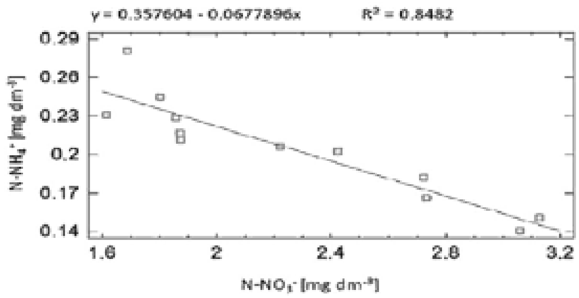

Fig. 6. Dependence of mean $N\text{-}NO_3^-$ on $N\text{-}NH_4^+$.

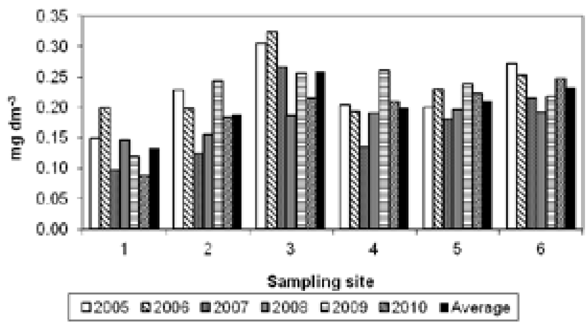

Fig. 7. Mean $N\text{-}NH_4^+$ concentrations depending on sampling site [mg dm^{-3}].

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Koncentrácia dusičnanového a amónneho dusíka v rozdielnych ekosystémoch

Súhrn

V priebehu rokov 2005–2010 sa hodnotil vplyv lesného, poľnohospodárskych a urbánnych ekosystémov na koncentrácie N-NO_3^-, N-NH_4^+ vo vodnom toku Čaradický potok. Vodný tok pramení v pohorí Pohronský Inovec a preteká územím okresov Zlaté Moravce a Levice. Na základe získaných výsledkov možno konštatovať, že najnižšie priemerné koncentrácie zo sledovaných anorganických foriem dusíka počas celého sledovaného obdobia boli v odberovom mieste lokalizovanom pod lesným ekosystémom Pohronský Inovec. Priemerná koncentrácia N-NO_3^- vo vodnom toku bola 2,26 mg dm^{-3}. Jeho najvyššia priemerná koncentrácia za celé monitorované obdobie sa zistila v mesiaci január a najnižšia v mesiaci august. Najvýraznejší vzostup koncentrácie N-NO_3^- sa zistil v mesiaci september v roku 2009, čo pravdepodobne súvisí s intenzívnou zrážkovou činnosťou pred odberom vzoriek (29. 9. 2009 napršalo 20,5 mm). V závislosti od odberového miesta boli maximálne priemerné koncentrácie N-NO_3^- v odberových miestach lokalizovaných pod urbánnymi ekosystémami (obce Kozárovce a Čaradice). Vzostup ich koncentrácie pod uvedenými obcami bol pravdepodobne zapríčinený sekundárnym zvýšením obsahu

dusičnanového dusíka, ktorý vznikal nitrifikáciou amónneho dusíka, nachádzajúceho sa v nevyčistených splaškových odpadových vodách (obce nemajú vybudované ČOV). Na zvýšení priemernej koncentrácie $N\text{-}NO_3^-$ vo vodnom toku za celé sledované obdobie participovali aj agroekosystém trvalých trávnych porastov (odberové miesto č. 2) a agroekosystém ornej pôdy (odberové miesto č. 4) nachádzajúce sa v povodí vodného toku. Vzostup pod uvedenými agroekosystémami bol však nižší ako pod urbánnymi ekosystémami. Analýzou rozptylu sa zistili štatisticky významné vplyvy všetkých troch kvalitatívnych faktorov (rok, mesiac a miesto odberu) na zmenu koncentrácií dusičnanového dusíka. Priemerná koncentrácia amónneho dusíka za celé monitorované obdobie reprezentovala 0,20 mg dm^{-3}. Najnižšie koncentrácie sa zaznamenali v zimnom a najvyššie v letnom období. Minimálna priemerná koncentrácia bola v mesiaci február a maximálna v mesiaci júl. V závislosti od odberového miesta jeho najvyššie priemerné koncentrácie počas celého sledovaného obdobia boli v odberových miestach lokalizovaných pod urbánnymi ekosystémami (obce Kozárovce a Čaradice). Analýzou rozptylu sa pre $N\text{-}NH_4^+$ potvrdil štatisticky vysoko preukazný vplyv kvalitatívnych faktorov mesiac a miesto odberu.

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