Evaluation of the concentration of inorganic nitrogen forms in the National nature reserve Čičov oxbow

Hodnotenie koncentrácie anorganických foriem dusíka v Národnej prírodnej rezervácii Čičovské mŕtve rameno

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Abstract

The aim of this study was to evaluate of concentrations of nitrate, ammonium and nitrite nitrogen in the water of National Nature Reserve Čičov oxbow during the years 2010 – 2013. The average concentration of nitrate nitrogen in water of National Nature Reserve during the whole monitored period was 3.42 mg*dm^{-3}. Maximum average concentration for the whole monitored period in the month of March and minimum in the month of November was found. Depending on the sampling sites it's the highest average concentrations were recorded in the first side distributary and the sampling place located in the northeastern part of the national nature reserve. Minimum average concentrations of $N\text{-}NO_3^-$ were recorded at sampling sites located in the first and second side distributary of reservation with the low water level. The average concentration of ammonia nitrogen during the whole monitored period was 0.15 mg*dm^{-3}. The highest average concentrations of $N\text{-}NH_4^+$ for the entire period were in summer period with maximum in month of June and minimum in month of February. Depending on the sampling place its highest average concentrations were in the sampling points located near the mouth of the Čiližsky channel in the northeastern part of reserve. The lowest average concentrations in the sampling point that was located at the first side distributary were measured. The average concentration of nitrite nitrogen during the whole monitored period represented 0.04 mg*dm^{-3}. The lowest average concentration of $N\text{-}NO_2^-$ for the entire monitored period was in month of January and the highest was in month of July. In terms of sampling place in all sampling sites during the entire period the same average concentration of nitrite nitrogen (0.04 mg*dm^{-3}) was measured.

Keywords: ammonium, nitrate, nitrite nitrogen, oxbow, surface water quality

Abstrakt

Cieľom práce bolo hodnotenie koncentrácie, dusičnanového, amónneho a dusitanového dusíka vo vode Národnej prírodnej rezervácie Čičovské mŕtve rameno počas rokov 2010 – 2013. Priemerná koncentrácia dusičnanového dusíka vo vode národnej prírodnej rezervácie za celé sledované obdobie bola 3,42 mg*dm^{-3}. Maximálna priemerná koncentrácia za celé sledované obdobie bola zistená v mesiaci marec a minimálna v mesiaci november. V závislosti od odberového miesta jeho najvyššie priemerné koncentrácie boli zaznamenané v prvom bočnom ramene a v odberovom mieste nachádzajúcom sa v severovýchodnej časti národnej prírodnej rezervácie. Minimálne priemerné koncentrácie $N\text{-}NO_3^-$ boli v odberových miestach, ktoré boli lokalizované v prvom a druhom bočnom ramene rezervácie s nízkou hladinou vody. Priemerná koncentrácia amónneho dusíka za celé sledované obdobie bola 0,15 mg*dm^{-3}. Najvyššie priemerné koncentrácie $N\text{-}NH_4^+$ za celé sledované obdobie boli v letnom období s maximálnou hodnotou v mesiaci jún a najnižšie v mesiaci február. V závislosti od miesta odberu jeho najvyššie priemerné koncentrácie boli zistené v odberovom mieste nachádzajúcom sa pod ústím Čiližského kanála a v severovýchodnej časti NPR. Najnižšia priemerná koncentrácia bola zaznamenaná v odberovom mieste, ktoré bolo lokalizované v prvom bočnom ramene. Priemerná koncentrácia dusitanového dusíka za celé sledované obdobie reprezentovala 0,04 mg*dm^{-3}. Najnižšia priemerná koncentrácia $N\text{-}NO_2^-$ za celé sledované obdobie bola v mesiaci január a najvyššia v mesiaci júl. Z hľadiska miesta odberu vo všetkých odberových miestach za celé sledované obdobie bola nameraná rovnaká priemerná koncentrácia dusitanového dusíka (0,04 mg*dm^{-3}).

Kľúčové slová: amónny, dusičnanový, dusitanový dusík, kvalita povrchovej vody, mŕtve rameno

Detailný abstrakt

Vzorky vody boli odoberané v Národnej prírodnej rezervácii Číčovské mŕtve rameno (47° 46' N 17° 43' E), ktorá sa nachádza na Podunajskej rovine v najviac zalesnenej časti Chránenej krajinnej oblasti, 30 km od Komárna smerom na Bratislavu. Odbery vzoriek vody sa realizovali pravidelne v mesačných intervaloch, vždy približne v polovici príslušného mesiaca, v rokoch 2010, 2011 a 2013. Odberové miesta sa určili tak, aby bolo možné zhodnotiť vplyv prírodných a antropogénnych zdrojov na kvalitu povrchovej vody. Určilo sa 8 odberových miest. Národná prírodná rezervácia Číčovské mŕtve rameno leží v suchej až mierne suchej oblasti s priemernou ročnou teplotou 9,9^{o}C, priemerný ročný úhrn zrážok je 550 – 600 mm. V odobratých vzorkách vody sa stanovil dusičnanový dusík ($N\text{-}NO_3^-$), amónny dusík ($N\text{-}NH_4^+$) a dusitanový dusík ($N\text{-}NO_2^-$). Na hodnotenie kvality povrchovej vody v odberových miestach podľa jednotlivých ukazovateľov sa použili hodnoty 90-teho percentilu (P90) vypočítané z nameraných hodnôt a následným porovnaním s im odpovedajúcou sústavou medzných hodnôt, ktoré sa uvádzajú v Nariadení vlády SR č. 269/2010 Z. z. Priemerná koncentrácia dusičnanového dusíka vo vode NPR Čičovské mŕtve

rameno za celé sledované obdobie reprezentovala 3,42 mg*dm^{-3}. Jeho podiel z celkového obsahu anorganického dusíka (N-NO_3^-, N-NH_4^+, N-NO_2^-) reprezentoval 94,43%. V závislosti od času odberu najvyššia priemerná koncentrácia N-NO_3^- za celé sledované obdobie bola v mesiaci marec (5,17 mg*dm^{-3}). V závislosti od miesta odberu jeho najvyššia priemerná koncentrácia sa zistila v odberovom mieste č. 6 (3,84 mg*dm^{-3}), ktoré bolo lokalizované v severovýchodnej časti národnej prírodnej rezervácie. Minimálne priemerné koncentrácie boli zaznamenané v odberovom mieste č. 5 (2,99 mg*dm^{-3}) a č. 7 (3,04 mg*dm^{-3}), ktoré sa nachádzajú v prvom a druhom bočnom ramene rezervácie s nízkou hladinou vody. Priemerná koncentrácia amónneho dusíka za celé sledované obdobie bola 0,15 mg*dm^{-3}. Jeho podiel z celkového obsahu anorganického dusíka (N-NO_3^-, N-NH_4^+, N-NO_2^-) reprezentoval 4,49%. Najvyššie priemerné koncentrácie N-NH_4^+ za celé sledované obdobie boli namerané v letnom období s maximálnou hodnotou v mesiaci jún (0,23 mg*dm^{-3}). Minimálna priemerná koncentrácia bola zistená v mesiaci február (0,09 mg*dm^{-3}). V závislosti od miesta odberu najvyššie priemerné koncentrácie amónneho dusíka boli zaznamenané v odberových miestach č. 2 (0,18 mg*dm^{-3}) a č. 4 (0,17 mg*dm^{-3}) a najnižšia v odberovom mieste č. 6 (0,13 mg*dm^{-3}). Priemerná koncentrácia N-NO_2^- za celé sledované obdobie bola 0,04 mg*dm^{-3}. Jeho podiel z celkového obsahu anorganického dusíka (N-NO_3^-, N-NH_4^+, N-NO_2^-) bol 1,08%. Najnižšia priemerná koncentrácia N-NO_2^- v priebehu celého sledovaného obdobia bola zistená v mesiaci január (0,02 mg*dm^{-3}) a najvyššia v mesiaci júl (0,06 mg*dm^{-3}). Z hľadiska miesta odberu vo všetkých odberových miestach za celé sledované obdobie bola nameraná rovnaká priemerná koncentrácia dusitanového dusíka (0,04 mg*dm^{-3}).

Introduction

Nitrogen is one of the basic macronutrients, but its presence in the waters depending on the form of occurrence and from its concentration can be toxic for the aquatic organisms and causes health problems (Imreová et al., 2013). Nitrates are the end product of biochemical oxidation of organically fixed nitrogen; occur in all types of water (Pošta, 2005). In biological transformations in waters liable to reduction to elemental nitrogen (denitrification) (Synáčková, 1996). By Jurík (2011), their concentration in the water varies in the range from 0.1 to 10.0 mg*dm^{-3}. In the surface water their important source are runoff from agricultural farmed land, fertilized by nitrogen fertilizers, industrial waste water and waste dump (Wittlingerová and Jonáš, 2004; Reddy et al., 2009; Zhu et al., 2009). In the natural waters, their concentration varies depending on the growing season (Noskovič, 1999). Maximum values reached in the spring, which represents 20-40% of the total annual erosion of nitrogen. Minimum values reached in autumn (Kvítek and Doležal, 2003; Kvítek, 2007). In the summer time on the contrary they are drained by vegetation, including forests. Any extreme nitrate concentrations in summer may be the result of surface runoff and erosion (Kvítek and Tippl, 2003). Ammonium nitrogen is product of microbial decomposition of organic nitrogen compounds, especially proteins in the reducing environment (Knapec and Časnochová, 2012). In the water is present in hydrated state (NH_3*H_2O) or in the form of NH_4^+ cations. Their proportional representation depends on the pH of the water. At pH < 8 is in the form of NH_4^+, at pH = 9.3 a temperature 20°C in a ratio 1:1, at pH > 10 in the form of undissociated toxic hydrate NH_3*H_2O (Hartman et al., 2005). Into natural waters is particular getting by discharge from fertilized fields, sewage and waste waters from the thermal treatment of coal (coking, gas, generating stations) (Molnárová et al., 2011). In natural waters in the presence of oxygen is very unstable. By biochemical oxidation (nitrification) passes to the nitrites and to the nitrate (Knapec and Časnochová, 2012). Nitrites as minerals not found in nature and in the unpolluted waters are in the minimum trace amounts. As an intermediate product in the process of nitrification are unstable and its higher levels are toxic to animals (Súdovský and Michalíková, 2009). Into the water are receiving by dissolving N_2O_3 from the atmosphere, which can be formed by oxidation of N_2 in electrical discharges in the atmosphere or is present in the exhaust gases of internal combustion engines. In the ground waters and surface waters is formed by biochemical oxidation of ammonium nitrogen. Higher concentrations can be found in blackwaters (of the order of tenths mg*dm $^{-3}$) and in the polluted waters (over 1 mg*dm $^{-3}$). Nitrites are important indicators of fecal pollution of waters (Molnárová et al., 2011).

Materials and Methods

National Nature Reservation Čičov oxbow (47° 46' N 17° 43' E) is left-side oxbow of Danube river, which is separated from the main stream by dum. Located is on the Podunajská rovina in the most wooded part of the protected landscape area, 30 km from Komárno direction to Bratislava. It is located in the cadastral area of Čičov and Kľúčovec at an altitude of 110 m, belongs to the river-basin of Danube. For the national nature reservation was announced in the year 1964 on the area 79.8715 ha, water area is 79.87 ha, protective zone is 55.25 ha. Čičov oxbow is considered to the largest lake in the oxbow of the river in Slovakia. After the break Danube dyke in 1899 was created. The average water depth is about 3 m, maximum measured depth was 7.5 m. Bank is divided by small peninsulas and bays. It is an important habitat for aquatic and wetland communities, which are characteristic for the meadow forests along Danube River with the 24 kinds of fish, over 100 species of birds and several other rare species of animals and plants (Hanušin, 2009). The area is particularly influenced by the flow of Danube, from which is oxbow water feed by subsurface seepage. Depending on the water level is surrounding area waterlogged, flooded at high states. From mid-summer the groundwater is declining because the evaporation dominates over precipitation. By the Žitný ostrov opens into the oxbow channel Vrbina – Medveďov and Čiližsky channel. Is an area of rain-snow runoff type, with the accumulation of water in the December – January, with high water levels in February – April. Geological structure consists mostly of Neogene clays – pannonian sediments of the lake, covered by quaternary Holocene alluvial sediments of gravel, sand, loess and flood waters. The basic quaternary elements are: fluvial – wetland sediments with organic additives and fluvial – alluvial sediments in the lowlands. In terms of soil conditions in the western part of the area are dominated clayey soil types and in the eastern part dominated clay-loam soil. The main soil types are: black soils carbonate, local peat soils on the carbonate alluvial sediments, and alluvial gley soils on the carbonate and non-carbonate sediments, mollic gley, mollic fluvisols and gley on the carbonate and noncarbonate alluvial sediments. Hydrogeological basis of the area consists from quaternary sands and gravels of alluvial. National nature reserve Čičov oxbow is located in dry to moderately dry areas with an average annual temperature of 9.9°C. The coldest month is January, with average monthly temperature - 2.1°C and the hottest month is July, with average monthly temperature 20.5°C. Territory is not only warmest zone, but is also one of the driest area of the Slovak republic. Average annual rainfall is 550 – 600 mm, the most precipitation falls in the months of May, June and July (average monthly rainfall 59.3 mm). Area is located in one of the windiest areas of Slovakia. Maximum speed of the wind and the windiest days occurs in winter and spring. The predominant wind direction is NW (Varga et al., 2006).

Collection and processing of samples

Collections of samples were realized regularly at the monthly intervals, always about in the half of the month during the years 2010, 2011 and 2013. Sampling place was determined in order to assess the impact of natural and anthropogenic source of surface water quality. Specifically, eight sampling points were indentified (Figure 1):

1. Sampling point – 47˚ 46' 7.17'' north latitude and 17˚ 43' 7.56'' east longitude, 110 m above sea level, located about 150 m from the mouth of the Číližský channel into the reserve. The average depth of the sampling point is 0.31m.
2. Sampling point – 47˚ 46' 6.51'' north latitude and 17˚ 43' 7.81'' east longitude, 104 m above sea level, is located 20 m near the mouth of Čiližský channel. The average depth of 0.37 m.
3. Sampling point – 47˚ 46' 5.88'' north latitude and 17˚ 44' 0.40'' east longitude, 107 m above sea level, located in the northeastern part of the national nature reserve. The average depth of the sampler is 0.43 m.
4. Sampling point – 47˚ 46' 4.04'' north latitude and 17˚ 44' 1.87'' east longitude, 111 m above sea level, located in the northeastern part, with an average depth of 0.43 m.
5. Sampling point – 47˚ 46' 2.09'' north latitude and 17˚ 44' 0.32'' east longitude, 111 m above sea level, the average depth of the sampling point is 0.50 m.
6. Sampling point – 47˚ 46' 0.02'' north latitude and 17˚ 43' 8.26'' east longitude, 111 m above sea level, similar to the 5. sampling site is located on the first side distributary. The average depth is 0.37 m.
7. Sampling point – 47˚ 46' 2.23'' north latitude and 17˚ 43' 4.45'' east longitude, 117 m above sea level, located on the second side distributary of the reservation, the average depth 0.39 m.
8. Sampling point – 47˚ 46' 3.77'' north latitude and 17˚ 43' 5.91'' east longitude, 117 m above sea level, located in the second side distributary of reserve with an average depth 0.39 m.

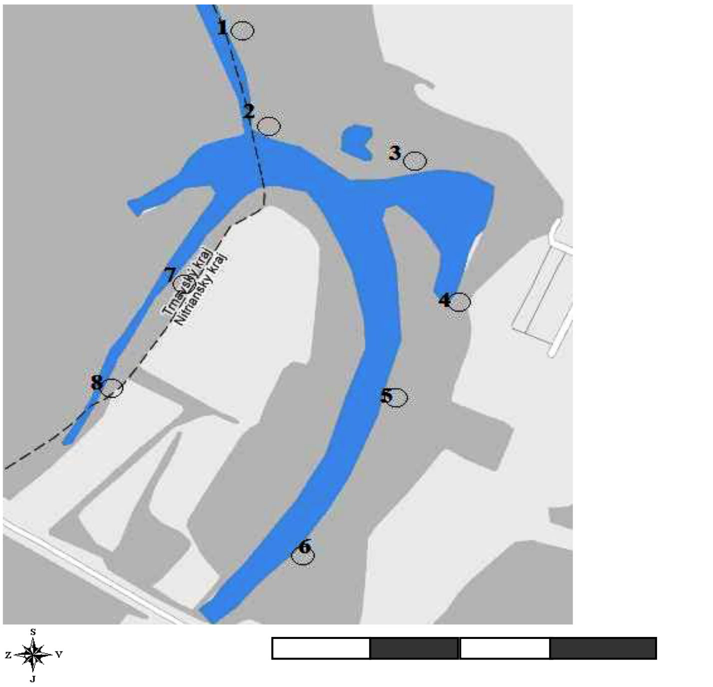

Figure 1. NNR Čičov ox-bow scale: 1 : 100 000

Obrázok 1. NPR Čičovské mŕtve rameno mierka: 1 : 100 000

In the collected water samples were determinate nitrate nitrogen (N-NO_3^-) – spectrophotometrically using WTW nitro spectral in concentrated sulfuric acid, the method is analogous to DIN 38402 part 51, ammonia nitrogen (N-NH_4^+) – spoectrophotometrically using idophenol blue – Berthol reaction, method is analogous to DIN 38402 part 51 and nitrite nitrogen (N-NO_2^-) – spectrophotometrically using sulphanilic acid and 1-naphthylamine, the method is analogous to DIN 38402 part 51. To assess the quality of surface water sampling in sampling points according to individual indicators the 90-th percentile (P90) were used. It was calculated from the measured values and the subsequent comparison with their corresponding system of limit values set out in Government Regulation No. 269/2010 Coll. The results were processed by mathematical-statistical methods (by program Statgraphics 5.0 plus).

Results and Discussion

The average concentration of nitrate nitrogen in water of National nature reserve Čičov oxbow during the whole monitored period represented 3.42 mg*dm^{-3} (Figure 2.). Its lower average concentration found Illyová (2010) in Podunajská nádrž Dolné Dubové in the year 2008 (0.63 mg*dm^{-3}). The slightly higher average concentration of N-NO_3^- (3.94 mg*dm^{-3}) in the water of gravel Rusovce in the years 2000-2007 Mucha et al. (2009) were found.

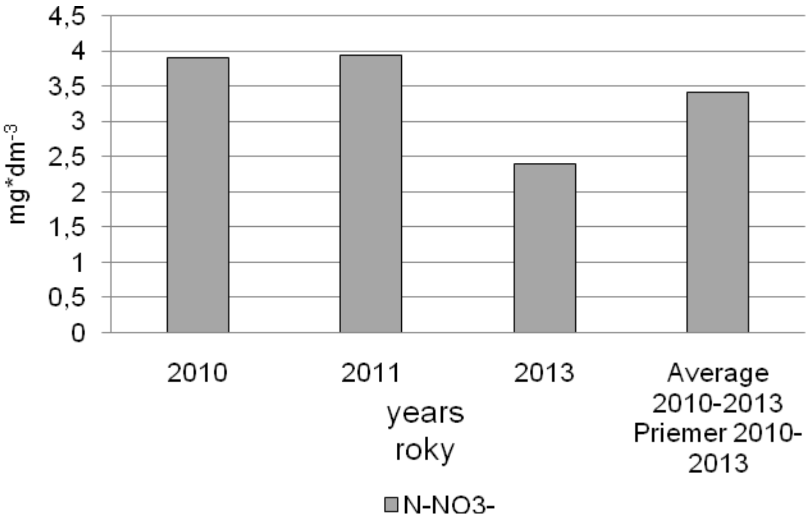

Figure 2. The average concentration of N-NO_3^- (mg*dm^{-3}) in the water of National nature reserve Čičov oxbow in the years 2010-2013

Obrázok 2. Priemerné koncentrácie N-NO_3^- (mg*dm^{-3}) vo vode Národnej prírodnej rezervácie Čičovské mŕtve rameno v rokoch 2010-2013

Its proportion of the total inorganic nitrogen (N-NO_3^-, N-NH_4^+, N-NO_2^-) represented 94.43%, which confirms that is the most represented from of nitrogen (Table 3.). From the average concentrations of N-NO_3^- depending on the time of sampling is apparent (Figure 3.) that his the highest average concentration for the whole monitored period was in March (5.17 mg*dm^{-3}). Can be assumed that higher concentrations of nitrate nitrogen in March could by caused by snowmelt and surface runoff of fertilizer from surrounding soil to the water of national nature reserve (near NPR is agriculturally cultivated arable land). In the spring time is surrounding area usually flooded and waterlogged. This agrees with the statement of Kvítek and Doležal (2003) and Kvítek (2007), that fluctuations of their concentrations is not followed immediately after period of application of mineral fertilizers, nutrients accumulates in the soil during autumn and winter period and rinsed out after accelerated water percolation during the melting period and immediately after snow melting. Its the highest average concentration in March also found Noskovič et al. (2011) in water of Alluvium Žitava. The higher concentration of nitrate nitrogen in water during the spring months also report Randall and Mulla (2001). The second highest average concentration of N-NO_3^- in July (4.49 mg*dm^{-3}) was recorded. This probably could be caused by the intense precipitation activities during the summer, when the monitored period in August was measured 238.70 mm rainfall. Atmospheric precipitation as possible source of nitrate nitrogen in summer period also mentioned Krupová (2010). Minimum average concentration of N-NO_3^- for the entire monitored period in November (2.36 mg*dm^{-3}) was measured, as the result of unfavorable conditions (low temperature of water) for the conduct of nitrification, there was decline in its concentration.

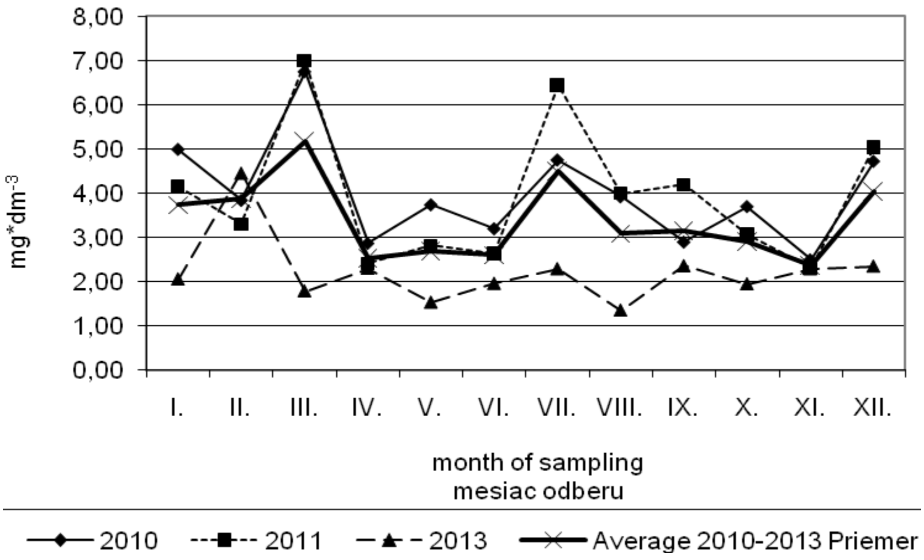

Figure 3. Average concentrations of N-NO_3^- ($mg*dm^{-3}$) depending on the time of sampling

Obrázok 3. Priemerné koncentrácie N-NO_3^- ($mg*dm^{-3}$) v závislosti od času odberu

From the graph of average concentrations of N-NO_3^- (Figure 4.) depending on the sampling sites indicate that the highest average concentrations in the water of National Nature Reserve Čičov oxbow in the first two studied years were found (2010, 2011) and the lowest in the last year of sampling of water (2013). The average concentrations of nitrate nitrogen indicate that between sampling sites during the reporting period there were no significant differences. It's the highest average concentrations at sampling sites no. 6 (3.84 $mg*dm^{-3}$), which was located in the northeastern part of the national nature reserve were observed. Minimum average concentrations of N-NO_3^- was in sampling sites no. 5 (2.99 $mg*dm^{-3}$) and no. 7 (3.04 $mg*dm^{-3}$), which were located in the first and second side distributary of reservation with low water level. Relatively shallow depth (0.50 – 0.39 m) does not create adequate conditions for the vertical temperature zonation of water during the year and for the spontaneous water circulation, which is makes by the temperature differences in the water column. In the monitored years during the summer period was the water superheated on average 24.6°C. Based on the above the decrease of nitrate nitrogen in those sampling sites according to Noskovič et al. (2011) can be justify by its intensive receives by phytoplankton and the low concentration of dissolved oxygen, which inhibits nitrification processes. According to Mucha et al. (2009) lower nitrate nitrogen content in the water can also be related with the reduction of nitrogen oxides in atmospheric precipitation.

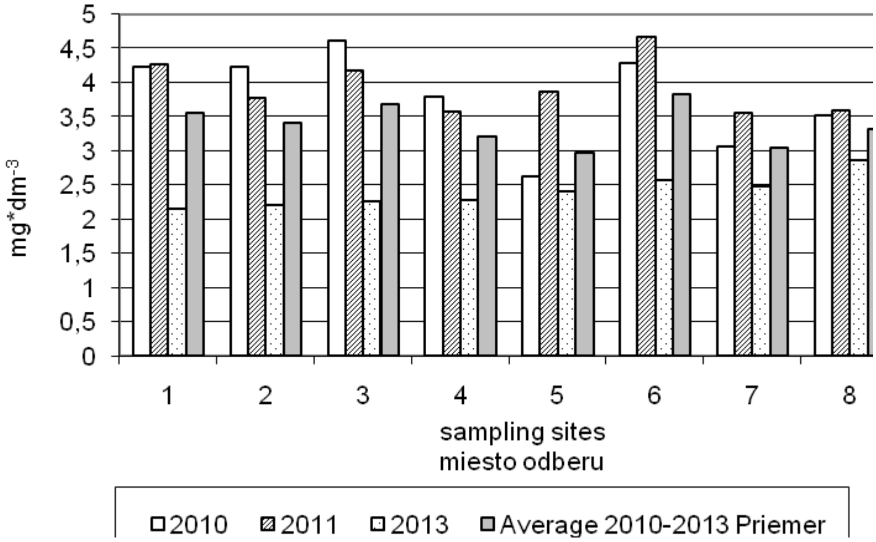

Figure 4. Average concentrations of N-NO_3^- (mg*dm^{-3}) depending on the sampling sites

Obrázok 4. Priemerné koncentrácie N-NO_3^- (mg*dm^{-3}) v závislosti od miesta odberu

When analyzing the variance of nitrate nitrogen was confirmed statistically high significant effect of the month of collection. Influence of sampling and sample month was statistically inconclusive. Statistically high significant interaction was between the year and month of collection and interaction year and takeoff. The interaction between the sampling month and place of collection was statistically significant (Table 1.).

Table 1. Analysis of variance concentrations of nitrate nitrogen

Tabuľka 1. Analýza variancie pre koncentrácie dusičnanového dusíka

Effect	The sum of squares	Degrees of freedom	Mean square	F	P
Year	0.476	1	0.567	3.581	0.06181
Month	28.26	12	2.489	18.479	0.0
Simple site	1.647	8	0.120	1.622	0.144823
Year*Month	36.876	12	3.345	25.576	0.0
Year*Simple site	4.437	8	0.659	4.691	0.000125
Month*Simple site	16.145	78	0.218	1.605	0.020395
Error	9.789	75	0.140		

F - value, P – value

In the regulation of the Government of the Slovak republic No. 269/2010 Coll. the recommended value for nitrate nitrogen is 5 mg*dm^{-3}. Calculated values of 90-th percentile (P90) of this indicator in all sampling locations were lower than the recommended value of government regulations (Table 5.).

Ammonium nitrogen compared with nitrate nitrogen was quantitatively less represented form of inorganic nitrogen. Its proportion of total inorganic nitrogen content ($N\text{-}NO_3^-$, $N\text{-}NH_4^+$, $N\text{-}NO_2^-$) represented 4.49% (Table 3.). The average concentration of $N\text{-}NH_4^+$ in monitored years varied from 0.13 mg*dm^{-3} (2011) to 0.18 mg*dm^{-3} (2013) and during the entire period was its average value 0.15 mg*dm^{-3} (Figure 5.). Higher average values for the period 1994-2004 measured Ženišova et al. (2005) in gravel pits Zlaté piesky (0.17 mg*dm^{-3}) and Kuchajda (0.20 mg*dm^{-3}).

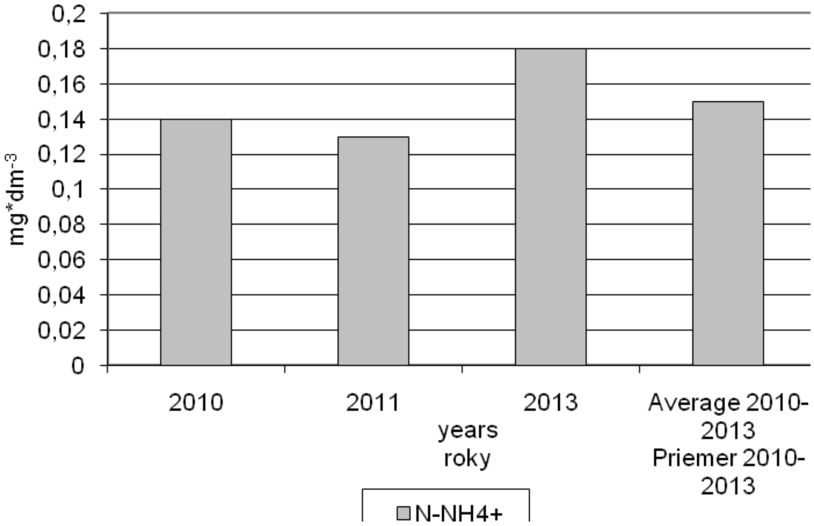

Figure 5. Average concentrations of $N\text{-}NH_4^+$ (mg*dm^{-3}) in the water of National Nature Reserve Čičov oxbow in the years 2010-2013

Obrázok 5. Priemerné koncentrácie $N\text{-}NH_4^+$ (mg*dm^{-3}) vo vode Národnej prírodnej rezervácie Čičovské mŕtve rameno v rokoch 2010-2013

The average concentrations of ammonia nitrogen shows (Figure 6.) that the highest average concentration for the whole monitored period were in summer, with maximum in June (0.23 mg*dm^{-3}). The increase of the concentration of ammonium nitrogen in the summer months in the water of Želečský stream also recorded Fialová et al. (2008) and Noskovič et al. (2011) in Alluvium Žitava. Similar trend in its seasonal dynamics were also found Pekárová et al. (2005) in the years 1992-2002, the highest concentrations of ammonia nitrogen in the river Hron – Šalková in June and July were found. Seasonal nature of the occurrence of ions of $N\text{-}NH_4^+$ in water referred Renwick et al. (2008). As the concentration of ammonium nitrogen is highly dependent on oxygen conditions can be stated that the higher values in summer, probably related to higher water temperatures and lower oxygen concentration, according to Tölgyessy and Melichová (2000) does not create favorable conditions for the nitrification to nitrite and nitrate nitrogen. Minimum average concentration of

$N\text{-}NH_4^+$ in the water of National nature reserve in February (0.09 mg*dm^{-3}) was measured.

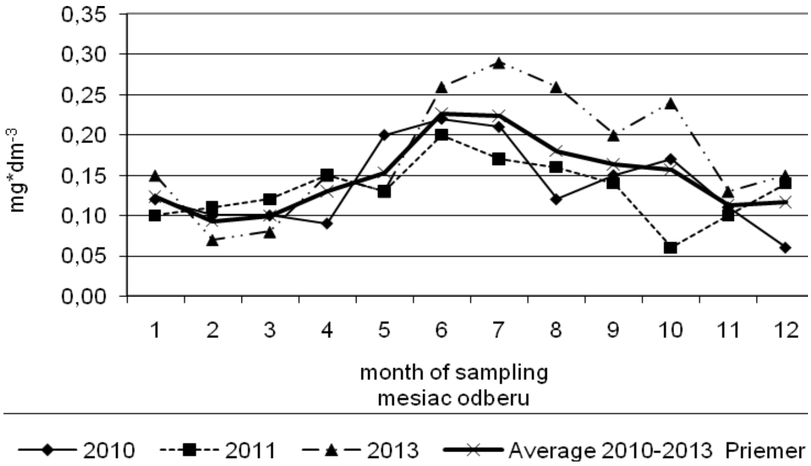

Figure 6. Average concentration of $N\text{-}NH_4^+$ (mg*dm^{-3}) depending on the time of sampling

Obrázok 6. Priemerné koncentrácie $N\text{-}NH_4^+$ (mg*dm^{-3}) v závislosti od času odberu

Highest average concentrations were in sampling sites no. 2 (0.18 mg*dm^{-3}) and no. 4 (0.17 mg*dm^{-3}) and the lowest in the sampling point no. 6 (0.13 mg*dm^{-3}), where the highest concentrations have been found of $N\text{-}NH_4^+$ (Figure 7.). This agrees with the statement of Noskovič et al. (2011) that under the favorable conditions the ammonia nitrogen oxidized to nitrate nitrogen.

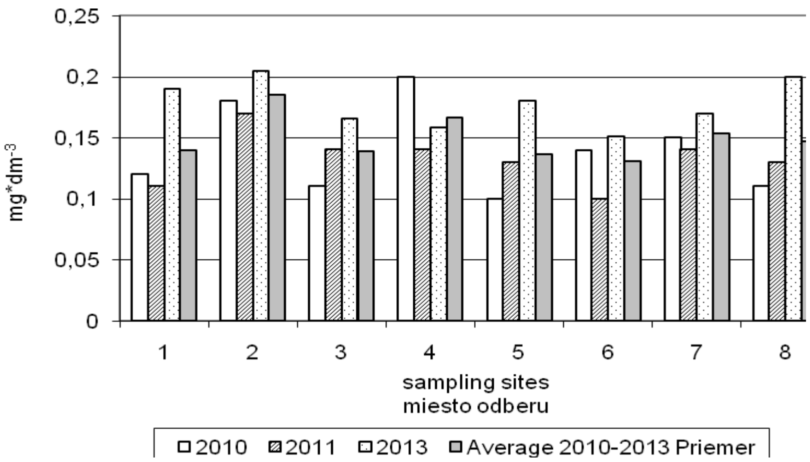

Figure 7. Average concentrations of $N\text{-}NH_4^+$ (mg*dm^{-3}) depending on sampling sites

Obrázok 7. Priemerné koncentrácie $N\text{-}NH_4^+$ (mg*dm^{-3}) v závislosti od miesta odberu

The analysis of variance for ammonium nitrogen indicates statistically highly significant effect of month and year, the impact of the sampling point was statistically inconclusive. It was significantly important in ammonia nitrogen interaction between the year and month of collection.

Table 2. Analysis of variance for concentrations of ammonium nitrogen

Tabuľka 2. Analýza variancie pre koncentrácie amónneho dusíka

Effect	The sum of squares	Degrees of freedom	Mean square	F	P
Year	0.001646	1	0.001646	0.2475	0.632735
Month	0.462701	12	0.048413	6.8708	0.0
Simple site	0.061763	8	0.007495	1.2894	0.413106
Year*Month	0.633749	12	0.05931	9.6652	0.0
Year*Simple site	0.031952	8	0.00527	0.7148	0.577901
Month*Simple site	0.403974	78	0.005811	0.8492	0.72693
Error	0.479689	75	0.006711		

F - value, P – value

In the regulation of the Government of the Slovak republic No. 269/2010 Coll. the recommended value for ammonia nitrogen is 1.0 mg*dm^{-3}. Calculated values of 90-th percentile (P90) of this indicator in all sampling locations were lower than the recommended value of government regulations (Table 5.).

Quantitative least represented form of inorganic nitrogen was nitrite nitrogen. Its proportion of the total content of inorganic nitrogen (N-NO_3^-, N-NH_4^+, N-NO_2^-) was 1.08% (Table 3.). The average concentration of N-NO_2^- in the reporting period ranged from 0.03 mg*dm^{-3} (2011) to 0.04 mg*dm^{-3} (2011 and 2013). During the whole period its average value was 0.04 mg*dm^{-3} (Figure 8.).

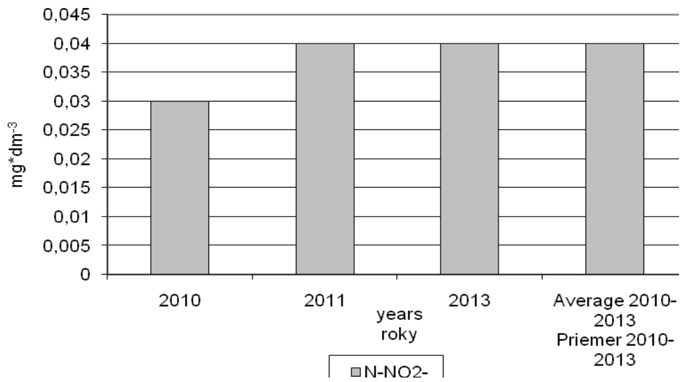

Figure 8. The average concentration of N-NO_2^- (mg*dm^{-3}) in the water of National nature reserve Čičov oxbow in the years 2010-2013

Obrázok 8. Priemerné koncentrácie N-NO_2^- (mg*dm^{-3}) vo vode Národnej prírodnej rezervácie Čičovské mŕtve rameno v rokoch 2010-2013

The lowest average concentration of N-NO_2^- during the whole monitored period was in January (0.02 mg*dm^{-3}) and the highest in July (0.06 mg*dm^{-3}). Since that month its average concentrations generally decreased gradually until the month of December (Figure 9.). By Radechovský et al. (2013) oxidation of nitrite nitrogen to nitrate nitrogen depends on the temperature and the actual concentration of dissolved oxygen in the water. Absolute the highest value of nitrite nitrogen in 2010 in the month of June (0.07 mg*dm^{-3}) was recorded. A similar seasonal dynamics of nitrite nitrogen in water of Alluvium Žitava also found Noskovič et al. (2011).

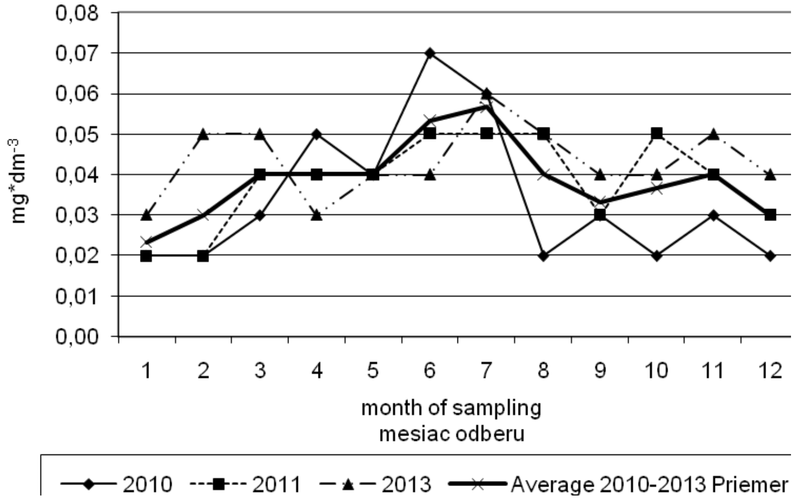

Figure 9. Average concentrations of N-NO_2^- (mg*dm^{-3}) depending on the time of sampling

Obrázok 9. Priemerné koncentrácie N-NO_2^- (mg*dm^{-3}) v závislosti od času odberu

In terms of sampling points in all sampling sites during the whole monitored period the same average concentration of nitrite nitrogen was measured (0.04 mg*dm^{-3}) (Figure 10.). Based on the above mentioned it can be concluded that in all sampling sites were the same conditions for the oxidation. According to Král et al. (2006), Malá (2008) and Súdovský and Michaliková (2009) the nitrification of water is affected by a number of factors such as temperature, pH, oxygen concentration, the concentration of nitrogen pollution and the occurrence of toxic substances. All of these factors inhibit nitrite oxidizing bacteria with predominant activity and the amount of ammonia oxidizing bacteria. For this reason there is an increase of nitrite in the water. High nitrogen load, particularly high concentration of ammonia and nitrite nitrogen can result in accumulate of nitrite by inhibition of nitrite oxidizing bacteria.

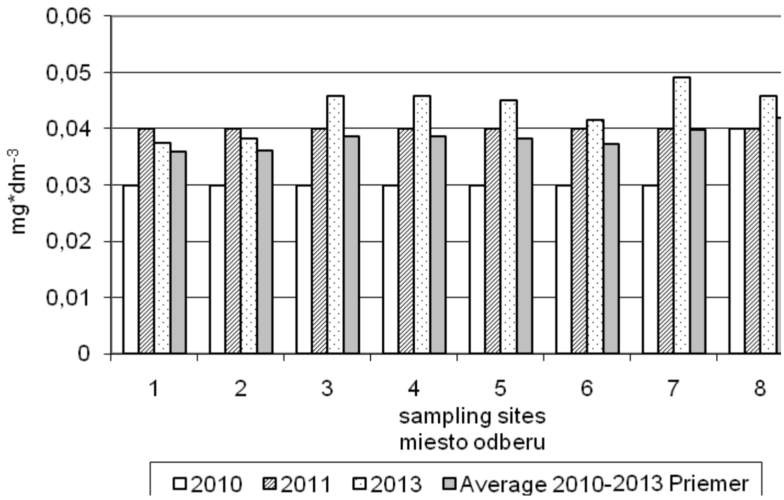

Figure 10. Average concentrations of N-NO_2^- (mg*dm^{-3}) depending on sampling sites

Obrázok 10. Priemerné koncentrácie N-NO_2^- (mg*dm^{-3}) v závislosti od miesta odberu

Table 3. Proportion of individual forms of nitrogen on the total amount of inorganic nitrogen

Tabuľka 3. Podieľ jednotlivých foriem dusíka na celkovej sume anorganického dusíka

Year	Sum of N-NO_3^-+N-NH_4^++ N-NO_2^- (mg*dm^{-3})	Percentages of the various forms of inorganic nitrogen in their amount		
		% N-NO_3^-	% N-NH_4^+	% N-NO_2^-
2010	4.08	95.83	3.43	0.74
2011	4.11	95.86	3.17	0.97
2013	2.62	91.60	6.87	1.53
Average	10.81	94.43	4.49	1.08

The analysis of variance for nitrite nitrogen that, statistically highly significant effect was the year and month of collection. Significantly important was the interaction between the year and month of collection. Impact of sampling sites are shown to be statistically inconclusive. Interactions between a takeoff, month sampling and the sampling sites were inconclusive in terms of statistics (Table 4.).

Table 4. Analysis of variance for concentrations of nitrite nitrogen

Tabuľka 4. Analýza variancie pre koncentrácie dusitanového dusíka

Effect	The sum of squares	Degrees of freedom	Mean square	F	P
Year	0.001571	1	0.001157	20.895	0.000019
Month	0.018416	12	0.001531	27.658	0.0
Sampling site	0.000171	8	0.000102	1.845	0.092713
Year*Month	0.016945	12	0.001336	24.138	0.0
Year *Sampling site	0.000827	8	0.000112	2.021	0.063422
Month*Sampling site	0.0053	78	0.000065	1.19	0.235634
Error	0.004082	75	0.000055		

F - value, P – value

In the regulation of the Government of the Slovak republic No. 269/2010 Coll. the recommended value for nitrite nitrogen is 0.2 mg*dm^{-3}. Calculated values of 90-th percentile (P90) of this indicator in all sampling locations were lower than the recommended value of government regulations (Table 5.).

Table 5. The calculated characteristic values of the 90th percentile (P90) for N-NO_3^-, N-NH_4^+ and N-NO_2^-

Tabuľka 5. Vypočítané charakteristické hodnoty 90-teho percentilu (P90) pre N-NO_3^-, N-NH_4^+ a N-NO_2^-

Calculated characteristic value	Sampling sites 1.	2.	3.	4.	5.	6.	7.	8.
N-NO_3^-	1.40	1.59	1.59	1.50	1.59	1.87	2.6	1.7
N-NH_4^+	0.06	0.06	0.05	0.07	0.06	0.05	0.05	0.05
N-NO_2^-	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02

Conclusion

Based on the obtained results during the whole monitored period, shows that the most represented form of the inorganic nitrogen was nitrate nitrogen, which is documented by the fact that its share of the total content of inorganic nitrogen represented 94.43%. Second quantitatively less represented form was ammonium nitrogen. Its proportion of the total content of inorganic nitrogen (N-NO_3^-, N-NH_4^+, N-NO_2^-) represented 4.49%. Quantitative the least represented form was nitrite nitrogen. Its proportion from the total content of inorganic nitrogen (N-NO_3^-, N-NH_4^+, N-NO_2^-) was 1.08%. Calculated values of 90-th percentile (P90) of N-NO_3^-, N-NH_4^+ and N-NO_2^- in all sampling locations were lower than the recommended value in the regulation of the Government of the Slovak republic No. 269/2010 Coll.

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