Concentrations of inorganic nitrogen forms in the water in different biotopes in the Nature Reserve Alúvium Žitavy

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Abstract

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Over the years 2006–2008, the concentrations of $N\text{-}NO_3^-$, $N\text{-}NH_4^+$, $N\text{-}NO_2^-$ were evaluated in dependence on sampling time and sampling site in the water of the Nature Reserve (NR) Alúvium (Aluvium) Žitavy, which is situated in the southwestern part of the Slovak Republic. On the basis of the results achieved, we can state that the mean concentration of nitrate nitrogen in the water of the Nature Reserve over the whole monitored period was 3.84 mg dm^{-3}. It represented 92.79% of inorganic nitrogen, the rest being represented by ammonium nitrogen and nitrite nitrogen. The highest mean concentration for the whole monitored period was found in March, and the lowest in June. In dependence on the sampling site, the highest mean $N\text{-}NO_3$ concentrations were found in the sampling sites. The sampling site No. 1 was situated on the inflow of the River Žitava into the Alluvium which proves that its important source is the river itself. The sampling site No. 4 was located in the narrowest part of Alluvium, where the river flows very quickly, oxygen is enriched, and therefore nitrification is more intensive. We found out statistically significant influence of the sampling year, month and site on the change in values of concentrations of this qualitative factor by analysis of variance. Ammonium nitrogen was quantitatively the second best represented by inorganic nitrogen. Of the total inorganic nitrogen it represented 5.53%. Its mean concentration over the whole monitored period represented 0.21 mg dm^{-3}. We recorded low concentrations of $N\text{-}NH_4^+$ over the whole monitored period in the winter months and the high ones in the months of July to September. In dependence on the sampling site we found out maximum mean $N\text{-}NH_4^+$ concentrations over the whole monitored period in the sampling sites with typical wetland ecosystems (sampling sites 2, 3, 5, 6). By analysis of variance for this indicator, it was found a statistically significant influence of the year, month and the sampling site on the change in its values. Nitrite nitrogen was the last represented from the monitored inorganic nitrogen forms. Of the inorganic nitrogen it represented 1.69%. Lower $N\text{-}NO_2^-$ concentrations, compared to $N\text{-}NO_3^-$ and $N\text{-}NH_4^+$, are probably related to its easy oxidation or reduction in waters. Minimum mean concentrations over the whole monitored period were in March, and April, and the maximum ones were in July. The sampling site had no statistical influence on the changes in $N\text{-}NO_2^-$ concentrations.

Key words

ammonium nitrogen, Nature Reserve, nitrate nitrogen, nitrite nitrogen, wetland

Introduction

Nitrogen and phosphorus are primary nutrients limiting productivity in wetlands (Vitousek et Howarth, 1991). Their increased concentrations in surface water are unfavourable because of their participation in the eutrophication (Wittlingerová and Jonáš, 2004), and they are usually responsible for changes to ecosystem function and structure (Carpenter et al., 1998).

The nitrogen cycling process in wetlands involves both aerobic and anaerobic conditions. Nitrogen in the form of ammonium (NH_4) is released from decaying plants and animal matter under aerobic and anaerobic conditions in the process known as ammonification. The ammonium then moves to the aerobic layer where it is converted to nitrate (NO_3). Nitrate not taken up by plants or immobilized by adsorption onto soil particles can leach downward with percolating water to reach the groundwater supply or move with surface and subsurface flow. Nitrate can also move back to the anaerobic layer where it may be converted to nitrogen gas by denitrification, a bacterial process, and subsequently returned to the atmosphere (*Biogeochemical cycles*, 2001). Jansson et al. (1994; cit. Vaikasas et Rimkus, 2004) found out that nitrogen removal in wetlands mostly depends on the denitrification and sedimentation, and that water retention time is the most important factor for the removal of nitrogen.

Material and methods

Research area

The Nature Reserve (NR) Alúvium Žitavy is situated in the cadastral land of the town Hurbanovo and the village Martovce in the southwestern part of the Slovak Republic (*Krajinno-ekologický plán obce Martovce*, 2006). Its area is 32.53 hectares, and it was established as the Nature Reserve in 1993. The Alluvium lies in the interperineal area of the River Žitava, from its present estuary of the River Nitra to the village of Veľký Vék (assumed air line) (Szabóová, 1989). It is closely adjacent surrounding agrocenosis with remainders of meanders of the original water course of the rivers Nitra and Žitava. There is an open water line of the canal with dense bank vegetation in the central part of the Reserve. The northern part is enlarged and there is continuous vegetation of riparian forest. Wetland ecosystems are situated mainly in terrain depression at the edge of the alluvium of the River Žitava (Bridišová et al., 2006).

Its larger part is flooded along the year, but especially in spring. There are different biotopes, aquatic, wetland and riverine vegetation. Riverine forests, particularly willow stands, almost along Alluvium provide suitable ecological conditions for nesting and roosting of avifauna. There are more than 76 bird species occurring in this area (*Prírodná rezervácia Alúvium Žitavy*, 2006). Furthermore is very important for conservation of fauna and flora genetic resources (*Štátny zoznam osobitne chránených častí prírody a krajiny Slovenskej republiky*, 2007).

The NR Alúvium Žitavy is a part of the Protected Landscape Area Dunajské luhy (*Krajinno-ekologický plán obce Martovce*, 2006). The aim is to protect biotopes of European importance (riverine willow-poplar and alder wood forests) and the species of European importance (*Proterorhinus* sp., *Rhodeus amarus*, *Gobio albipinnatus*, *Bombina bombina*, *Lutra lutra*, *Citellus citellus*, species of national importance *Microtus oeconomus*) (Bridišová et al., 2006). Concurrently, NR Alúvium Žitavy is a part of the Special Protection Area SKSPA 005 Dolné Považie to which also belongs the proposed habitat of European importance 0159 Alúvium Žitavy (*Krajinno-ekologický plán obce Martovce*, 2006). The rare species of avifauna are for example *Ardea* sp., *Remiz* sp., *Botaurus* sp., *Circus* sp., *Anas* sp., *Acrocephalus* sp., *Charadrius* sp., *Locustella* sp., etc. In term of protected flora, there are *Leucojum aestivum* growing almost over the whole area of the NR and *Nuphar lutea* on water surface. *Ceratophyllum* sp., *Lemna minor* and *Lemna trisulca* form a typical green cover on the water surface. Along the interperineal area of the River Žitava, there is wetland vegetation from which communities of *Phragmites australis*, *Typha latifolia*, *Carex* sp. and *Scirpus* sp. are dominant (*Prírodná rezervácia Alúvium Žitavy*, 2006).

Sampling and processing of the material

Water sampling was carried out from the 6 sampling sites in the NR. The water samples were taken regularly during the years 2006–2008, on the 15th day of each month. The sampling sites were proposed to obtain the best possible data for the evaluation of changes in N-NO_3^-, N-NH_4^+ and N-NO_2^- concentrations in water in dependence on the sampling time and site. We have established the following 6 sampling sites:

Sampling site No. 1 (47°51'88" N, 18°09'89" E, 121 m a.s.l.) – inflow of the River Žitava into the Alluvium. *Phragmites australis* and *Salix* sp. grow along the River Žitava. The average depth is 0.32 m.

Sampling site No. 2 (47°51'92" N, 18°09'25" E, 111 m a.s.l.) and **No. 3** (47°51'83" N, 18°09'25" E, 117 m a. s. l.) – these sampling sites are typical wetland ecosystems. There is a very dense vegetation of *Phragmites australis* and *Salix* sp. in this part of the NR. The water surface is covered by *Lemna minor*. Water in these sites flows very slowly, and the height of its level change is in dependence on weather during the year. The average depth is 0.30 m.

Sampling site No. 4 (47°51'58" N, 18°08'38" E, 129 m a.s.l.) – it is situated near a bridge on a road to the village of Martovce. It is also the narrowest part of Alluvium; where the water in the River Žitava flows most rapidly. There is a typical vegetation of *Phragmites australis*, *Salix* sp. and *Alnus* sp. on the banks of the River Žitava. The average depth is 0.40 m.

Sampling site No. 5 (47°51'09" N, 18°07'99" E, 116 m a.s.l.) and **No. 6** (47°50'81" N, 18°07'67" E, 121 m a.s.l.) – typical wetland ecosystems. Here, the River Žitava flows out of its watershed during rapid snow melting in spring and intensive precipitation events in summer. In comparison with the second and the third sampling site, the river floods the whole depression between the two slopes. In dry summer the water level decreases by about a few metres. This part of Alluvium is represented mainly by an open water area. *Typha latifolia*, *Phragmites australis*, *Alnus* sp. and *Salix* sp. grow along the river. The water surface in sampling site No. 6 is covered with *Lemna* sp. forming a typical green cover. Beyond this sampling site, the River Žitava flows into the River Nitra. The average depth in sampling site No. 5 is 0.26 m and 0.39 m in the sampling site No. 6.

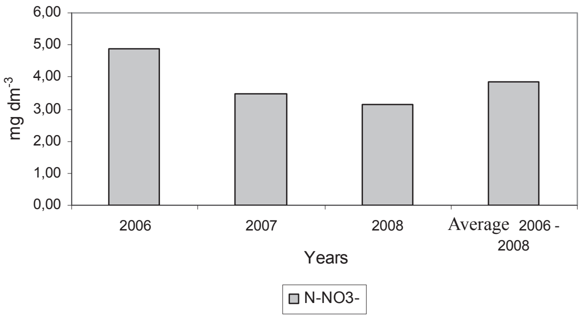

Fig. 1. Mean N-NO_3^- concentrations in years 2006–2008

The N-NO_3^- concentrations in the samples collected were determined spectrophotometrically, using a WTW nitrospectral in concentrated sulphur acid. The concentrations of N-NH_4^+ were determined spectrophotometrically, using indophenolic blue. The concentrations of N-NO_2^- were determined spectrophotometrically, using sulphanilic acid and 1-naphthylamine.

The results achieved were graphically processed in term of the sample time and the sampling site, and then processed statistically. All the statistical analyses were carried out using the statistic system Statgraphics Plus 5.0. The basic statistical characteristics of each data file were calculated for all monitored indicators (see Table 1). The statistical differences based on three qualitative factors (sampling year, sampling month, sampling site) were tested by analysis of variance. LSD test for testing statistical contrasts was used at significance level of 95% and 99%.

Results and discussion

From the obtained data it follows that N-NO_3^- represented 92.78% from the three monitored inorganic nitrogen forms. This result confirms that the nitrate nitrogen is the final nitrogen form in decomposition of organically fixed nitrogen, and that it is stable in aerobic conditions in water. The mean concentration over the whole monitored period was 3.84 mg dm^{-3} (see Fig. 1). The maximum mean concentration over the whole monitored period was obtained in March (9.22 mg dm^{-3}) and in this month in March 2006, the highest nitrate nitrogen concentration was measured (14.90 mg dm^{-3}). We suppose that the growth in N-NO_3^- concentration could be caused by increasing intensive nitrification of water of the NR and low N-NO_3^- uptake by autotrophic organisms. Nosković et al. (2007) examining water reservoirs Veľká Richňava, Malá Richňava and Veľká Vindšachta, also found out higher N-NO_3^- concentrations in spring season (spring circulation) than in summer (summer stagnation). Sebíň et al. (2007) found out maximum nitrate concentrations in surface water during snow melting in spring, minimum concentrations from June to August followed by a slight increase in autumn months. Rising nitrate concentrations during snow melting in spring and heavy autumn rains were also recorded by Růžičková et al. (2000) in lothic ecosystems situated in the catchments of the rivers Vydra and Křemelné (NP Šumava). The lowest N-NO_3^- concentration over the whole monitored period was recorded in July (1.36

Table 1. Basic statistical characteristics

Indicator	N-NO_3^-	N-NH_4^+	N-NO_2^-
Unit	mg dm^{-3}	mg dm^{-3}	mg dm^{-3}
Count (n)	216.00	216.00	216.00
Average	3.84	0.21	0.06
Minimum	0.30	0.03	0.02
Maximum	16.10	0.76	0.40
Median	3.10	0.17	0.04
Mode	2.20	0.11	0.03
Variance	8.981	0.016	0.003
Standard deviation	2.997	0.127	0.057
Standard error	0.204	0.009	0.004
Range	15.80	0.73	0.38
Coefficient of variation (%)	78.041	60.403	95.154

mg dm^{-3}). In comparison with the increase in spring, the drop of N-NO_3^- concentration was probably caused by inhibition of nitrification due to insufficient amount of oxygen dissolved. Sufficient content of dissolved oxygen as well as N-NO_3^- consumption by primary producers in photosynthesis are important for nitrification process. LELLÁK and KUBÍČEK (1991) state similar conclusions. Content of dissolved oxygen is reduced by microorganisms during organic matter decomposition, and it entail reduction of nitrification speed (*A wetlands monitoring program*, 2004). KUNÍKOVÁ et al. (2005) also found out a decrease of N-NO_3^- concentration in summer in Anakonda wetland (an abandoned meander of the River Latorica). Mean N-NO_3^- concentrations in dependence on a sampling time are illustrated in Fig. 2.

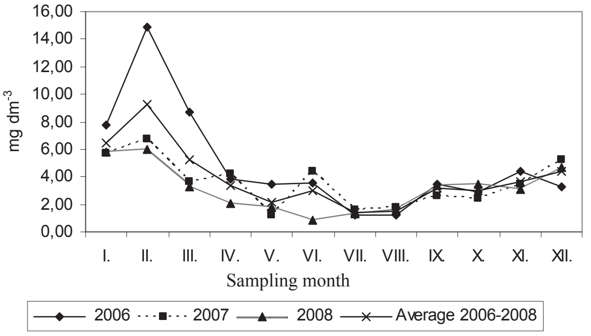

Fig. 2. Mean N-NO_3^- concentrations depending on sampling time

In term of the sampling site (see Fig. 3), the highest mean N-NO_3^- concentrations were in the sampling sites No. 1 (5.00 mg dm^{-3}) and No. 4 (4.66 mg dm^{-3}). We can suppose that the River Žitava is an important source of N-NO_3^- because the sampling site No. 1 is situated on the inflow of the River Žitava into the Alluvium. High mean N-NO_3^- concentrations in the sampling site No. 4 could be caused by favorable conditions for nitrification (sufficiency of dissolved oxygen as a result of water aeration because the river in this sampling site reaches maximum flow velocity). The lowest mean concentration was in the sampling site No. 6 (2.89 mg dm^{-3}). Low concentrations were recorded also in the sampling sites No. 2, 3 and 5 (wetland ecosystems). There is dense wetland vegetation on the banks and water surface is covered by common duckweed. Organic matter from dead vegetation cumulates in organic sustains in water. Content of dissolved oxygen in water decreases in consequence of oxidation of organic substances and results in nitrification inhibition. This is characteristic mainly for the summer season. In addition, it is known that phytoplankton intensively uptakes nitrate nitrogen from water.

All three qualitative factors (sampling year, month and site) were associated statistically with significant differences in amounts of N-NO_3^-. We found out a highly significant difference between the first and the second sample year (2006–2007) and another between the first and the third sample year (2006–2008). In dependence on the sampling site, highly significant difference was found between the sampling site No. 1 and No. 2, 3, 5 and 6, due to different biotopes in the individual sampling sites. Another high significant difference was between sampling sites No. 2 and 4, No. 4 and 6. We recorded negative correlation between nitrate nitrogen and ammonium nitrogen (r = –0.328) which is related to instability of ammonium nitrogen in oxidized conditions in water (N-NH_4^+ is easily biochemically oxidated to N-NO_3^-).

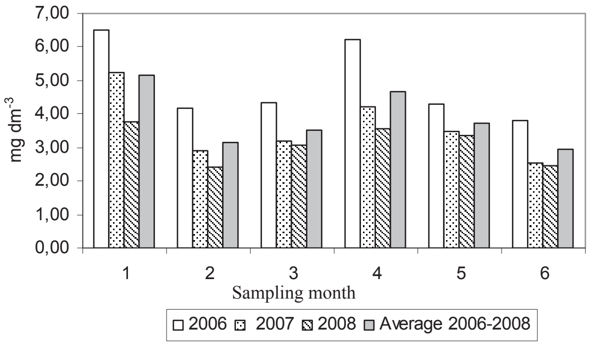

Fig. 3. Mean N-NO_3^- concentrations depending on sampling site

Ammonium nitrogen represented 5.53% from the monitored inorganic nitrogen forms. Its mean concentration over the whole monitored period was 0.21 mg dm^{-3} (see Fig. 4). Mean concentrations of N-NH_4^+ in Anakonda wetland ranged from 0.155 to 0.575 mg dm^{-3} (KUNÍKOVÁ et al., 2005). From diagram showing mean N-NH_4^+ concentrations (see Fig. 5) it follows that low mean concentrations were in winter, minimum mean concentration of N-NH_4^+ was in February (0.12 mg dm^{-3}), and high concentrations in July and September (0.26 mg dm^{-3}). We suppose that the decrease in N-NH_4^+ concentration occurred in consequence of a low water temperature in the Nature Reserve in winter when organic nitrogen substances were not microbially decomposed. Subsequently, ammonia ions released. Ammonia ions originate during decomposition of organic maters containing nitrogen, and their occurrence is linked with lack of dissolved oxygen in water (BRVENÍK, 2002). In waters with sufficient supply of dissolved oxygen, organic matter is oxidized by microorganisms to nitrate ions which are easily acceptable by plants (KLEE, 1990; cit. ADAM et al., 2001). Dependence between mean N-NH_4^+ values and mean dissolved oxygen values over the whole monitored period is showed in Fig. 6. From this figure it follows that N-NH_4^+ concentrations increased with decreasing dissolved oxygen content, mainly in the summer period when water in Alluvium had higher temperature and low content of dissolved oxygen. Negative correlation between N-NH_4^+ concentration and dissolved oxygen content in water (r = –0.47) was revealed by statistical evaluation.

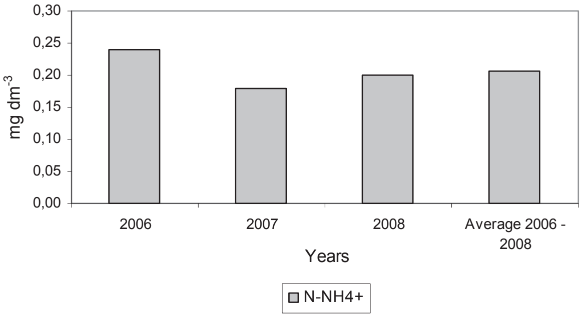

Fig. 4. Mean N-NH_4^+ concentrations in years 2006–2008

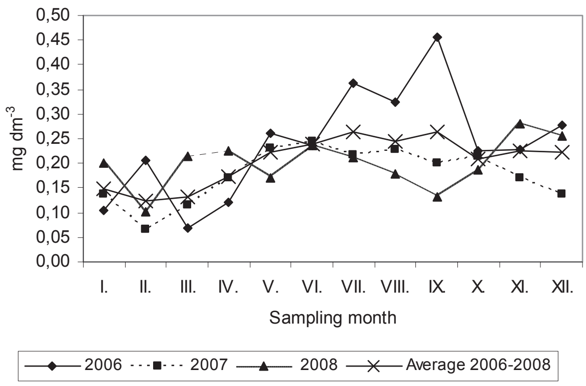

Fig. 5. Mean N-NH_4^+ concentrations depending on sampling time

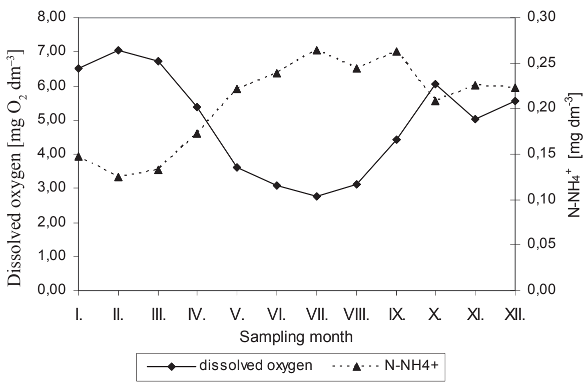

Fig. 6. N-NH_4^+ concentration and concentration of dissolved oxygen

N-NH_4^+ concentrations were gradually rising from March to the summer period. Their maximum was recorded in the already mentioned months of July and September. Kuníková et al. (2005) states that oxygen from nitrates is used during increased demands on oxygen. The increase in ammonium ions content in water can also be seen, as a result. Chalupová and Janský (2007) found out maximum concentrations of ammonium nitrogen in the summer period when N-NH_4^+ release was higher than its oxidation to nitrate nitrogen, as well as after vegetation season when the decomposition rate progressively increases. According to Patten (1990) ammonium nitrogen is the main inorganic nitrogenous compound in natural wetland ecosystems, and its values can reach 1–2 mg dm^{-3} in summer.

In dependence on the sampling site, we found out that maximum mean N-NH_4^+ concentrations over the whole monitored period in the sampling sites are typical wetland ecosystems (No. 2, 3, 5, 6) (see Fig. 7). We recorded the highest mean N-NH_4^+ concentrations in the sampling site No. 5 (0.33 mg dm^{-3}) and No. 6 (0.31 mg dm^{-3}) in 2006. Increased N-NH_4^+ concentrations in these sampling sites can be connected with over-reproduced phytoplankton forming algal bloom on water surface and consuming dissolved oxygen in water for own respiration. Huge amount of necrotized organic matter have accumulated at the bottom. With decomposition of organic matter, N-NH_4^+ was released, but it was not further oxidized, in consequence of low values of dissolved oxygen. The tendency in N-NH_4^+ concentrations was opposite to N-NO_3^- concentrations in the sampling sites. Beňačková and Noskovič (2004) also found out that the low content of dissolved oxygen caused the increase in N-NH_4^+ concentrations and decrease in N-NO_3^- concentrations.

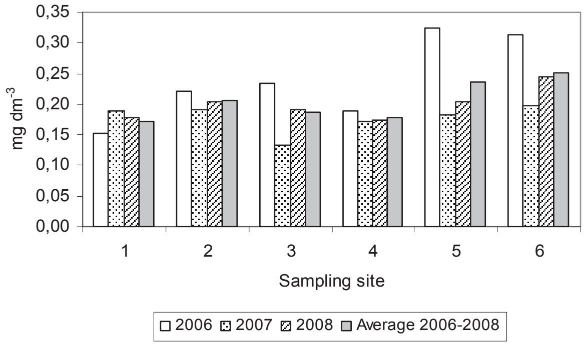

Fig. 7. Mean N-NH_4^+ concentrations in depending on sampling site

Similarly to N-NO_3^-, we found out that the sampling year, month and site statistically significantly influence values change of N-NH_4^+. In term of the sampling time, high significant difference was between the first and the second sampling year. In term of the sampling site, a high significant difference was between the sampling site No. 1, 4 and No. 6.

Nitrite nitrogen represented 1.69 % from the monitored inorganic nitrogen forms. Mean annual concentration of nitrite nitrogen over annual monitored years was gradually falling and its mean concentration over the whole monitored period represented 0.06 mg dm^{-3} (see Fig. 8). Compared with previous forms of inorganic nitrogen, low N-NO_2^- concentrations are related to be instable in waters, and they can be easily oxidized or reduced biochemically chemically (Pitter, 1990), nitrification is especially fast in presence of oxygen (Hudec, 1996). Mean N-NO_2^- concentrations in dependence on the sampling time are illustrated in Fig. 9. From this figure it follows that over the whole monitored period, the lowest mean N-NO_2^- concentration was in March and April (0.04 mg dm^{-3}) and the highest one in July

(0.10 mg dm^{-3}). We found out absolutely highest values of N-NO_2^- from May to July 2006. Rapid increase in N-NO_2^- concentrations in these months in 2006 can be explained by high water and air temperatures. Kabelková-Jančárková (2002) states that in the summer, bacteria oxidizing nitrites grow less quickly than bacteria oxidizing ammonium. Nitrite production in biofilms is higher than its consumption. Therefore nitrites diffuse from biofilm into water when their concentration increases. According to Buday (2002), low concentrations of oxygen reduce the activity of nitrifying bacteria, whereby bacteria oxidizing nitrites react more sensitively than bacteria oxidizing ammonium.

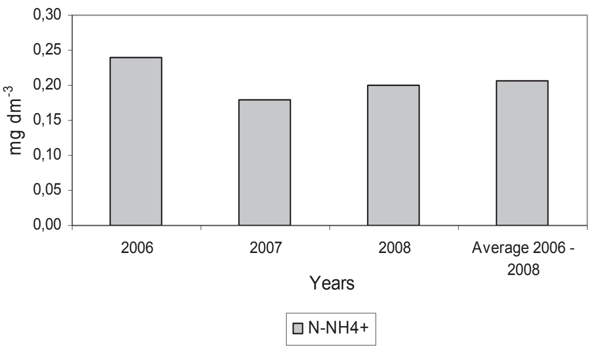

Fig. 8. Mean N-NO_2^- concentrations in years 2006–2008

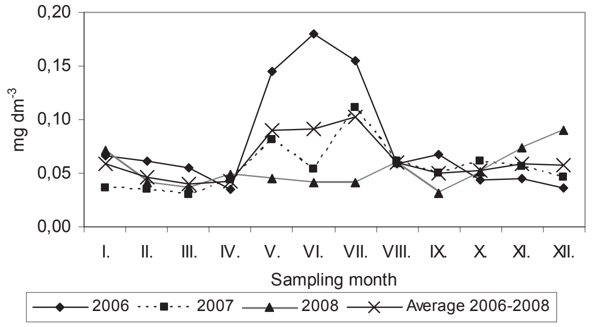

Fig. 9. Mean N-NO_2^- concentrations depending on sampling time

Mean N-NO_2^- concentrations in dependence on the sampling site are illustrated in Fig. 10. The highest mean concentrations in the individual sampling sites were measured in 2006 (0.06–0.09 mg dm^{-3}). Over the whole monitored period, the lowest mean concentration (0.06 mg dm^{-3}) was in all sampling sites, except for the sampling site No. 5 in which the highest mean concentration over the whole monitored period was found out (0.07 mg dm^{-3}).

Statistical evaluation revealed that N-NO_2^- values were influenced significantly only by sampling year and month. Similarly to N-NO_3^- and N-NH_4^+, statistically high significant differences were between 2006 and 2007 and between 2006 and 2008.

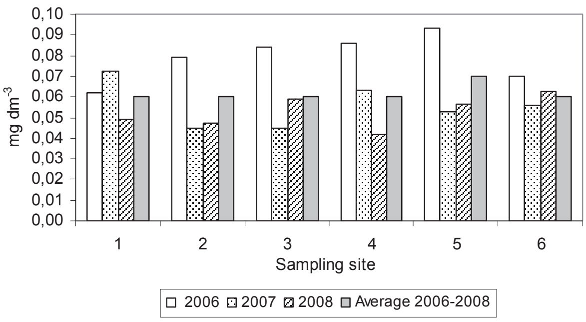

Fig. 10. Mean N-NO_2^- concentrations depending on sampling site

Acknowledgement

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Koncentrácie anorganických foriem dusíka vo vode v rôznych biotopoch Prírodnej rezervácie Alúvium Žitavy

Súhrn

V priebehu rokov 2006 –2008 sa vo vode Prírodnej rezervácie Alúvium Žitavy, ktorá sa nachádza v juhozápadnej časti Slovenskej republiky, hodnotili koncentrácie N-NO_3^-, N-NH_4^+, N-NO_2^- v závislosti od času a miesta odberu. Na základe získaných výsledkov môžeme konštatovať, že priemerná koncentrácia dusičnanového dusíka vo vode PR za celé sledované obdobie bola 3,84 mg dm^{-3}. Z anorganického dusíka predstavoval až 92,79 %, zvyšok tvorili amónny a dusitanový dusík. Najvyššia priemerná koncentrácia za celé sledované obdobie bola zistená v mesiaci marec a najnižšia v mesiaci jún. V závislosti od odberového miesta boli najvyššie priemerné koncentrácie N-NO_3^- v odberových miestach č. 1 a 4. Odberové miesto č. 1 sa nachádzalo na vtoku rieky Žitavy do alúvia, čo dokumentuje, že jeho významným zdrojom je samotná rieka. Odberové miesto č. 4 bolo lokalizované v najužšom mieste Alúvia, kde rieka prúdi najrýchlejšie, obohacuje sa o kyslík a preto nitrifikácia prebieha intenzívnejšie. Analýzou rozptylu sme zistili štatisticky významný vplyv všetkých troch kvalitatívnych faktorov (rok odberu, mesiac odberu, miesto odberu) na zmenu koncentrácií tejto formy dusíka. Kvantitatívne druhou najviac zastúpenou formou anorganického dusíka bol amónny dusík. Z anorganického dusíka predstavoval 5,53 %. Jeho priemerná koncentrácia za celé sledované obdobie bola 0,21 mg dm^{-3}. Nízke koncentrácie amónneho dusíka sa zaznamenali v zimných mesiacoch a vysoké v mesiacoch júl až september. V závislosti od odberového miesta najvyššie jeho

priemerné koncentrácie za celé sledované obdobie boli v odberových miestach mokraďového charakteru (odberové miesto č. 2, 3, 5, 6). Analýzou rozptylu pre tento ukazovateľ sme zistili štatisticky významný vplyv roka, mesiaca a miesta odberu na zmenu jeho hodnôt. Kvantitatívne najmenej zastúpenou anorganickou formou dusíka bol dusitanový dusík. Z anorganického dusíka reprezentoval 1,69 %. Jeho priemerná koncentrácia za celé sledované obdobie bola 0,06 mg dm^{-3}. Nižšie koncentrácie $N\text{-}NO_2^-$ v porovnaní s $N\text{-}NO_3^-$ a $N\text{-}NH_4^+$ súvisia pravdepodobne s jeho ľahkou oxidáciou resp. redukciou vo vodách. Za celé sledované obdobie boli najnižšie priemerné koncentrácie $N\text{-}NO_2^-$ v mesiacoch marec a apríl, najvyššia v mesiaci júl. Odberové miesta nemali štatistický vplyv na zmenu koncentrácií dusitanového dusíka.

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