

Influence of Organic Ammonium Derivatives on the Equilibria Between of NH_4^+ , NO_2^- and NO_3^- Ions in River Waters

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Abstract

The braking effect of the ammonium derivatives on the natural aquatic environment varies dramatically with the number and nature of organic radical substitutions at nitrogen atom, particularly with their structure, composition and genesis. The most common discrepancy in their toxic effect are showing the natural and synthetic amines. For instance, the values of the maximum allowable concentration (MAC) of the derivatives of the natural origin for drinking water exceed the MAC of the synthetic ones by two orders. On the other hand, it has been found out that 1-naphthylamine (1-NA) inhibitory effect is associated to its toxicity. The Diethylamine (DEA) braking impact on the nitrification process is effectively lower than that of the toxicity. Our experiments show that the carbon-radicals of organic amines act as reducing agents. It is found that DEA decomposition leads to a high NH_4^+ ions (approx. 3.8 mg/L ammonium nitrogen) concentration in river water samples. By laboratory simulations two types of fixations by microbial organisms have been established: 1) absorption-desorption, the hydromicrobiotic reaction to ammonium (HMBRA) at the instantaneous increase of the concentration of ammonium ion in the river water (so-called shock/stress effect); 2) nitrogen fixation stimulated by a certain concentration (0.05mg/L) of a 1-NA and other amines.

Introduction

Ammonium ion from water basins is a product largely derived from the degradation of organic matter of protein origin, which manifests a selective toxic effect (Britto et al. 2001, Britto, and Konzucker, 2002, Müller et al., 2006). Similar to carbon dioxide and methane, it is a final product of living organisms and substrates of combustion/fermentation processes. The presence of ammonium in natural water stimulates the increase of algae and heterotrophic autotrophic bacteria activities [Daum, et. al., 1998, Lin, et al., 2010, Dalton et. al., Arp, et al., 2002, Do, et al., 2008]. As a result of the degradation and decarboxylation (Snider and Wolfenden 2000, Zamora et al. 2015, Perez et al. 2017) of protein amino acids, the aquatic environment contains a large variety of organic ammonium derivatives, in which hydrogens partially or totally are replaced by different radicals. Beside the amines of natural origin, ones produced by chemical synthesis are very often present in water basins. Unfortunately, the amines of industrial origin (especially aromatic ones) are more toxic and more difficult to decompose in aquatic environment, constituting emerging pollutants in biological treatment plants. Pollution is becoming even more dangerous if the industrial azo-dyes in anaerobic environment are reduced to aromatic amines (Newsome et al. 1991, Greim et al. 1998, Poste et al. 2014, Ramos et al. 2002, Chen et al. 2009, Pinheiroa et al. 2004).

One should mention the toxicity amplification of cationic surfactants (SAS-Ct) with the increasing of water hardness (Lewis 1992). On the other hand, the increase of CaCO_3 concentration is leading to the reactivation of emerging cationic organic pollutants with a negative impact, which presence is due to discharging of the insufficiently purified waste water in rivers. The braking phenomenon of nitrification in the presence of CaCO_3 is characteristic for the river sections polluted with waste water of the cities from

where the cationic SAS and other emerging substances are discharged (Spataru et al. 2015, Spataru et al. 2017, Spataru et al. 2018). The starting point of our study has been dedicated to the analysis of their influence on the concentrations of various nitrogen forms and to the behavior of a numbers of nitrogen-linked radicals. Another aspect of this study has been dedicated to the highlighting the cationic surfactants (SAS-Ct) impact on the urban sewage nitrogen forms in natural water models with and without CaCO_3 . Consequently, a previously developed model of the arrangement of SAS on the surface of calcium carbonate nanoparticles has been taken into account (Cui2010, Cui2012). The model is based on (I) the fixation of the anionic part and further decomposition of the SAS-Ct • SAS-An complex, and (II) on the passage of the cationic part in solution, increasing the braking activity of ammonium derivatives (Spataru et al. 2015, Spataru et al. 2017, Spataru et al. 2018).

The investigated samples, containing SAS-Ct and SAS-An, were tested in aqueous solutions with and without CaCO_3 by the UV spectroscopy method (Spataru et al. 2017). Both UV spectra and laboratory simulations reveal the change due to the addition of calcium carbonate. Thus, the surface of the calcium carbonate in the absence of ammonium ion chooses SAS-An only; however, upon adding an aqueous solution of NH_4^+ , the surface of the CaCO_3 particles may adsorb both the anionic and cationic SAS.

The amines from natural waters, being, in principle, derivatives of the ammonium with the hydrogen replaced by various organic radicals, break the oxidation of ammonia and nitrite ions decomposition in aquatic basins (Ramos et al. 2002, Tanaka et al. 2009, Ahmed et al. 2010). Under these circumstances, the study of the behavior of stable soluble forms (NH_4^+ , NO_2^- , NO_3^-) in natural water basins is crucial in discovering new insights of the environmental medium aspects (Ramos et al. 2002, Chen et al. 2009). Particularly, the concentration dynamics of stable soluble nitrogen species in water, investigated by the laboratory simulations, may serve as sensitive indicators for the organic matter composition and its transformations in aquatic environment (Sandu, M., et al., 2007, Spataru 2011, Spataru 2015, Spataru 2017, Spataru 2018, Spataru 2019). The determination of the influence of variable amounts of different ammonium derivatives on the dynamics of stable soluble nitrogen species (NH_4^+ , NO_2^- , NO_3^-), along with the redox processes in the aquatic environment, are the target of this study.

Materials And Methods

The used physicochemical methods here have been previously described (ISO 7150-1:2001, ISO 8466-1:1990, SR ISO 7890-3:2000, SM SR EN 26777:2006, Sandu 2014) and are based on the sensitivity of the soluble nitrogen species (NH_4^+ , NO_2^- , NO_3^-) to the influence of the microbial enzymatic system, which, in turn, is a function of the chemical composition of natural water and, in particular, of organic matter from natural water (river, lake, sewage basin, etc.). All parameters of the models were similar (temperature, atmospheric pressure, daylight) to those of the studied aquatic objects from which the water sample was collected for the laboratory model. At the initial stage of the laboratory simulation process a small amount of NH_4^+ was added. The water of the Nistru River at Vadul-lui-Voda section was used. NH_4Cl solution was added to the river water samples, in order to achieve two concentrations of about 3 mg/L

and about 6 mg/L of ammonium ions. The reference sample contained only ammonium ions, while the working samples contained also amines from chemical industry waste (1-NA, DPA) and that resulting from the decomposition of proteins plus their degradation products (DEA). Both amines used in the chemical industry and those resulting from natural processes of protein and amino acid decomposition were investigated at different concentrations: lower, permissible and higher ones. Due to the variable toxicity of the amines, a conditional reference was used as maximum admissible concentration (MAC). Laboratory models were investigated, respecting the minimum recommended amount of water sample in glass vessels and were examined under natural lighting and temperature conditions, away from direct sunlight. The analysis of natural waters was accomplished according to the ISO methods (ISO 7150-1:2001, ISO 8466-1:1990, SR ISO 7890-3:2000, SM SR EN 26777:2006). Sample testing was completed using the HACH DR/2500 Spectrophotometer and UV spectroscopy using Perkin Elmer Lambda 25.

Results And Discussions

The ammonia and its derivative environmental amines are physiological products, which are released through a wide range of bacteria catalytic systems (Müller et al. 2006, Daum et al. 1998, Lin et al. 2010, Dalton 1977, Arp et al. 2002, Do et al. 2008, Snider and Wolfenden, 2000, Zamora et al. 2015, Perez et al. 2017, Newsome et al. 1991, Greim et al. 1998, Poste et al. 2014) and natural redox processes.

The dynamics of ammonium oxidation may serve as an indicator of the state and potential of self-purification of the aquatic environment. The ammonium ion concentration decreases dramatically during the first day, but then it increases on the second day after the initiation of laboratory simulations (Figs 1 and 2). These water models with similar behavior do not depend on the concentration of NH_4^+ or of 1-NA of about the MAC levels, as one can observe on Figs. 1 and 2. It should be noted that this effect is also common for both reference and other model samples. The above mentioned effect was analyzed within a large range of 1-NA concentrations: 0.025, 0.05, 0.1, 0.25 and 0.5 mg/L, which are 0.5; 1; 2; 5 and 10 MACs, due to its special impact (Spataru 2011) on the aquatic environment.

The analysis of the NH_4^+ concentration difference (in mg/L) for various number of days was performed. Four sets of values of concentrations were considered: 1) the difference between the values of the initial concentration (C_0) and that obtained after one day (C_1), i.e. ($C_1 - C_0$); 2) the difference between the values obtained after two days of experience and the initial ones, ($C_2 - C_0$); 3) the difference between the values obtained after two days of experience (C_2) and those after one day of experience (C_1), ($C_2 - C_1$); as well the difference of the values ($C_3 - C_1$). Figure 3 depicts the differences in ammonium ion concentrations between the starting day (C_0), of the laboratory simulations and the next few days, 1) ($C_1 - C_0$); 2) ($C_2 - C_0$); 3) ($C_2 - C_1$) 4) ($C_3 - C_0$), as a function of the 1-NA concentrations when the initial ammonium ion concentration was 3 mg/L. **Fig.3.** The difference of ammonium ion concentrations:

One can observe from Fig. 3 and Table 1 that the total soluble mineral forms of nitrogen is increasing during the period of nitrogen fixation (starting on second day and continuing on third day). Thus, the increase of ammonium nitrogen is not due to other soluble nitrogen species sources of the river water. A

similar growth in the ammonium ion concentration was detected in the river water experiment within laboratory models with the initial concentration of 2 mg/L NH_4^+ for the same 0.05 mg/L concentration of 1-NA (Spataru2011,Sandu 2007). A large peak on curves of the NH_4^+ species concentration versus the surfactant concentration, between the first and the third day, was observed within the series with initial concentration of 3 mg/L NH_4^+ . This peak is maximal and more pronounced for the sample with 0.05 mg/L of 1-NA concentration (Figs. 1 and 3), comparing to other 1-NA concentrations of 0.5, 0.25, 0.1 and 0.025 mg/L. Therefore, the concentration of 0.05 mg/L 1-NA stimulates nitrogen-fixing species in river waters. In our previous experiments, the concentration of ammonia nitrogen increased by more than 50% of the initial NH_4^+ concentration in the sample with the similar concentration of 1-NA after three days of experiment (Spataru 2011). Also, the NH_4^+ concentration increase did not stop after three days and continued for about ten days for the natural water samples of the spring period (Spataru2011). In natural waters the bio-chemical equilibrium is valid throughout the whole time of experiment involving microbial populations with nitrogen fixation properties (by adding NH_4^+). Some microbial populations use ammonium nitrogen compounds for its growing and another use them for maintaining their live through redox process of nitrogen species. The fixation and redox processes of nitrogen-containing compounds take place together, stimulating the selection of microbial population. Fig.3 and Fig. 4 show that in all the samples the adsorption of ammonium ions prevails essentially over other bio-chemical equilibria during the first day of the experiments and can be estimated by the C1-C0 difference. In the second day, the NH_4^+ concentration exceeded the initial value, then decreased (Figs.1 and 2),for the samples of 0.25, 0.1, 0.05 and 0.025 mg/L, which indicated to a drop of the ammonium concentration due to possible adsorption and redox processes. The allure of the curve for reference sample is similar. As it was above mentioned, the increase of the NH_4^+ concentration is maximum for 0.05 mg/L of 1-NA sample (Curve 4 in Fig. 3). Simultaneously, beside the stimulation of nitrogen fixation, the consumption/oxidation of ammonium ions is less significant during the third day comparing to the second day. The decreasing of nitrogen of ammonium ion fixation and the increasing of the redox process is more significant after the day third of the experiment (Fig. 1), leading to a permanent decreasing of ammonium ions concentration for all the samples. On the sixth day, the rate of the NH_4^+ oxidation/consumption process exceeds that of nitrogen fixation. The ammonium ion concentration dynamics as a function of the 1-NA concentration (Fig. 3 and Fig. 4) do point out to the fact that the nitrogen fixation process is still continuing.

The analysis of the natural water model behavior as a function of 1-NA concentration at initial concentration of 6 mg/L NH_4^+ was performed. Three sets of model experiments were selected: 1) the difference between the values of the initial concentrations (C0) and those obtained after one day (C1) of laboratory simulations, (C1 – C0); 2) the difference between the values obtained after two days of experience (C2) and those after one day (C1), (C2 – C1); 3) the difference between the values after two days of experience and initial values; (C2 – C0) (Fig. 4). One can observe that in the first two days at the concentration of 6 mg/L NH_4^+ , the 1-NA concentration has a well-defined impact. The sharp peak of NH_4^+ concentration (Fig. 3), due to the significant effect of nitrogen fixation at 0.05 mg/L of 1-NA

concentration, is not characteristic in the case for the samples with the initial concentration of 6 mg/L NH_4^+ (Fig. 4). In the first two days the nitrogen fixation/adsorption and then desorption take place.

One can observe from the Fig. 4 that the curves 1, 2, and 3, showing the difference between initial, first and second days of the NH_4^+ ions concentration, should asymptotically intersect by the increasing of the 1-NA concentration. By extrapolating the curves 1, 2 and 3 of Fig.4, the concentration of 1-NA at which the modification of NH_4^+ concentration will no longer take place, was obtained. The three curves intersect at the point with the value of 1-naphthylamine concentration of 0.70 (± 0.035) mg/L. Therefore, the value of 1-NA concentration, at which it is supposed to stop completely the processes connected to the biochemical production and adsorption of the NH_4^+ , due to its toxicity, is equal to about 0.70 mg/L. One can conclude that the process of decreasing of ammonium concentration on the first day after the initiation of laboratory simulations, and its increasing on the second day, caused by aquatic microorganisms, could be called the hydro-micro-biotic reaction to ammonium (HMBRA). It is worth to compare the total mineral nitrogen in samples with the initial concentration of 3mg/L and 6mg/L NH_4^+ (Table 1). The increase in the amount of ammonium ions in water samples leads to the shift of biochemical equilibria in the direction of decreasing the nitrogen fixation. From the Table 1, one can observe that during the second day of the experiment in the sample of 0.05 mg/L 1-NA, containing only 3mg/L NH_4^+ in initial concentration, the process of nitrogen fixation takes place. Indeed, the concentration of ammonium ions in this model increases during the second day while in the reference sample at the same day its concentration decreases. On the other hand, the behavior of the ammonium ion concentration, during the second day of the experiments, in the samples with 6 mg/L of NH_4^+ with and without 0.05 mg/L 1-NA, is similar (Table 1). Therefore, the increase of the NH_4^+ initial concentration from 3 to 6 mg/L leads to the suppression of nitrogen fixation processes.

Table1 Total soluble mineral nitrogen concentration in river water models

Test time	Reference test, initially 3mg/L NH ₄ ⁺	0.05mg/L 1-NA and 3mg/L NH ₄ ⁺ initially	Reference test, initially 6mg/L NH ₄ ⁺	0.05mg/L 1-NA și 6mg/L NH ₄ ⁺ initially
0 day	3.33	3.31	6.13	5.93
1 day	2.86	2.67	2.93	3.98
2 days	2.72	3.14	4.53	4.18
5 days	2.60	3.29	3.25	3.32
6 days	2.56	2.65	3.58	3.46
7 days	2.52	2.61	3.75	3.54

The increase of C1-C0, C2-C1 and C2-C0 parameters and the concentration of total mineral nitrogen in water (Fig. 3) for 3 mg/L NH₄⁺, contrary to the case of 6 mg/L NH₄⁺ (Fig. 4), shows that the nitrogen fixation takes place only for lower concentration of ammonium ions at the same concentration of 0.05 mg/L of 1-NA. The registered decrease of total nitrogen concentration in the model with 3 mg/L of initial NH₄⁺ during the 6th and 7th days and the absence of this effect in the model with 6 mg/L of initial NH₄⁺ (Allen, et al. 2005, Davidson et al. 2007, Domingues et al. 2011, Hollibaugh et al. 2011, Yang et al. 2017) leads to the supposition that the bacterial plankton responsible for the nitrogen adsorption is suppressed at higher concentration of ammonium ions. From the Figs. 1-4 one can also observe that the HMBRA braking reaction, nitrogen fixation, NO₃⁻ reduction to NH₄⁺ and denitrification occur with the increase in the 1-NA concentration due to its toxic effect at high and medium concentrations.

Nitrate ion converting by bacteria directly into ammonia is the type of dissimilatory nitrate reduction to ammonium (DNRA) process more common in soil, wetlands and lake sediments. (Jones et al. 2017, Nizzoli et al. 2010, Rutting et al. 2011). Nevertheless, it looks similar to the conditions without special insulation of the model (e.g. conditions that would cause an insignificant oxygen deficit), where the aquatic microorganisms take advantage of the possibility of using oxygen from nitrate to synthesize directly ammonium ions without intermediate nitrite ions. Nitrite ion is one of the most toxic components for the aquatic environment. Definitely, the NO₃⁻ → NH₄⁺ redox transformation, excluding the formation of intermediate NO₂⁻ ions, is most convenient both energetically and environmentally.

Dynamics of NH₄⁺ concentration in Figs 1, 2 and of NO₂⁻ concentration in Fig. 5 and their comparative analysis point out the influence of 1-NA concentration to the river water purification process. These

figures show that at lower concentrations of 1-NA than MAC and even at its equal concentrations, the ammonium oxidation occurs harder than in the reference sample. If the concentrations of 1-NA exceed the MAC values, the braking ammonium oxidation is more pronounced. In other words, the NO_2^- oxidation into NO_3^- proceeds more slowly than the formation of NO_2^- by NH_4^+ oxidation, leading to the increase of NO_2^- concentration. At the same time, the NO_2^- accumulation becomes gradually more pronounced as the concentration of 1-NA increases.

By comparing the dynamics of the ammonium ion concentration with that of the formation of the nitrite ions, one can observe that the natural aquatic environment shows a high sensitivity to the presence of 1-naphthylamine even at its much lower concentrations than MAC. On the other hand, at the equal concentrations of the components in the Fig. 1, 2 and 5, the dynamics of the NH_4^+ and NO_2^- displays an equilibrium between these two ions in our models, namely the converting of ammonium ions into nitrite ones and vice versa. There are no doubts that the oxidation/transformation of various forms of organic carbon in a complicate equilibrium mechanism in natural waters is related with the oxygen consumption from nitrate and nitrite. From Fig. 5 one can conclude that the oxidation of ammonia and intermediate forms of nitrogen oxidation leads finally to the nitrate formation in the river waters. Thus, the decrease in the NO_2^- concentration at the 20th day is noticeable within the laboratory simulations with 1-naphthylamine in both 3 mg/L and 6 mg/L NH_4^+ initially containing samples. Generally, the increase of ammonium ions and 1-naphthylamine concentrations causes a significant influence on the aquatic natural water bio-chemical equilibria, leading to the increase in the duration of redox intermediate processes of NO_2^- formation (Fig. 5). The dynamics of nitrite concentration variation in these laboratory models points out to a clear accumulation of soluble oxygenated nitrogen compounds, e. g. to a synchronization growth of heterotrophic and autotrophic bacteria (Philis al.2002, Sandu 2007, Spataru 2011).

The study of the behavior of nitrogen species equilibria in natural waters in the presence of diethylamine (DEA) is relevant not only because of its presence in the industrial waste, but also because DEA is assimilated by aquatic microorganisms. Comparing with above presented data, our simulations show a completely different picture of the bio-chemical and redox equilibria in the presence of DEA (Fig. 6a and 6b). First of all, it should be mentioned the large difference between the MAC values of the DEA samples, compared to 1-NA ones (almost larger by two orders). Samples with a relatively low concentration of 1-NA (between 0.025 and 0.5 mg/L) and those containing large amounts of DEA (between 2.0 and 20.0 mg/L) correspond to the same MAC values (between 0.5 and 10 respectively).

The content of the nitrogen amine is much larger in DEA samples than in 1-naphthylamine ones. DEA is an aliphatic amine of natural origin and 1-NA is an aromatic amine of synthetic origin. Therefore, the decomposition, oxidation, and assimilation of DEA occurs naturally much easier (see Fig. 5 and 6) than those of 1-NA, which impact on generated redox processes is influenced by lower activity of bacterial enzymes and/or microbial populations. For 1-NA, the NH_4^+ oxidation is delayed during the first days of

experiments (Figs. 5 and 6) comparing with the reference sample, even if after this time the NO_2^- concentration in analyzed models is larger compared to the reference one. One can expect that this oxidation delay comes merely from the effect of braking NO_2^- oxidation. In the case of DEA, (Fig. 6), there is a delay of both the oxidation of NH_4^+ and the subsequent oxidation of NO_2^- , compared to the reference sample. One can see from the Fig. 6 that the presence of low DEA concentration (2.0 mg/L) leads to an increase of the nitrite amount and, therefore, to the greater rate of its formation, while the large content of DEA (20 mg/L) causes the decrease of the NO_2^- amount both in 3 and 6 mg/L of NH_4^+ containing samples. It looks like the low DEA amount causes an enzymatic activation in which most of organic carbon species, including DEA carbon radicals, are present in the river water samples, while the increasing of DEA concentration (20 mg/L) leads to the growing of the amine nitrogen participation into the updated oxidation/reduction mechanism, which involves its converting in the ammonium form.

Remarkably, the behavior of the NH_4^+ in the presence of DEA during first days of the experiment follows a similar path as in the presence of 1-NA. In fact, during first day the NH_4^+ content gets lower, and then on the second day its concentration increases considerably. For the 20.0 mg/L containing DEA sample, the difference between the ammonium nitrogen concentration values on 10-13 days and 20-42 days of the experiment is about 3.5 mg/L or slightly higher. Note that the maximum amount of nitrogen obtained at the decomposition of 20 mg of DEA would be comparable (about 3.8 mg/L). Presumably, for the concentration of 20 mg/L DEA added in natural water samples, the increase of ammonium nitrogen within the interval of 20-42 days of the experiment is commensurable with the sum of the nitrogen amount resulted in various natural processes, as the nitrogen fixing (especially during the 10-13 days) and its accumulation at the complete decomposition of DEA (between 20-42 and 10-13 days). For the experiment with 2 mg/L DEA, the decrease of NH_4^+ is concomitantly accompanied by the formation of NO_2^- , as in the reference sample. However, for the samples containing 20 mg/L DEA, the decrease of NH_4^+ concentration and the increase of NO_2^- concentration are delayed in the samples with both initial NH_4^+ concentrations (Fig. 6). It is possible that in these samples the oxidation of organic carbon takes place by the participation of oxygen from nitrite and nitrate ions due to a relative oxygen deficit in aquatic samples. Here, there is a definite shortage of oxygen, as evidenced by decreasing the amount of NO_2^- and NO_3^- in the first ten days of experiments. However, after 10 days, the NO_3^- concentration has an increasing tendency, up to 50 days after simulation. Interestingly, the NO_2^- concentrations in the samples, for both 3 mg/L and 6 mg/L of NH_4^+ initial concentration with 20.0 mg/L of DEA, becomes moderately high even after 50 days of the experiment (Fig. 6a and 6b).

The industrial waste product in natural waters is often diphenylamine (DPA). Figs 7 and 8 display the braking effect on the NH_4^+ to NO_2^- oxidation in water containing both 0.05 mg/L and 0.5 mg/L DPA in initial models. In contrast to 1-NA models of river water samples, the models of DPA manifest a low influence of its concentration on the NH_4^+ oxidation process. In the sample containing 0.5 mg/L DPA

(curve 2 in Fig. 7), the oxidation of NH_4^+ is somehow slower than that in the samples with 0.05 mg/L DPA (curve 3 of Fig. 7).

For natural water models with 3mg/L of the initial concentration of NH_4^+ , the difference between the sample with 0.05 mg/L and 0.5 mg/L DPA is completely surprising due to the increase in the NH_4^+ concentration on the day 16th. Presumably, the shift from 0.05 mg/L to 0.5 mg/L of DPA leads to the reversal of the oxidation time of NH_4^+ for these two samples. The confirmation of this phenomenon is detailed in Table 2 (see the modifications from the days 14-16th to 19th day). During the period, where the NH_4^+ oxidation dynamics has noticeable changes, each of the stable soluble nitrogen species (NH_4^+ , NO_2^- and NO_3^-) has a different behavior in each of the model samples (Table 2). In the sample containing 3mg/L of NH_4^+ and of 0.05mg/L DPA initial concentration, after the days 14th and 15th there is an increase of NH_4^+ concentration, while the NO_2^- concentration is decreasing, and the NO_3^- concentration is relatively constant (Fig. 7, curves 3 and 5, and Table 2).

The concentration of total soluble nitrogen (TSN) on the day 16th exceeds by about 1 mg/L this quantity for the other days (14, 15 and 19). This difference is similar to the increase of NH_4^+ concentration compared with the previous days (14, 15). Due to the increase in the concentration of NH_4^+ , there is a delay in its oxidation dynamics in the sample with 3mg/L of initial concentration and 0.05mg/L DPA compared to the sample with the same NH_4^+ concentration and 0.5mg/L DPA. In the model containing 6 mg/L of NH_4^+ and 0.05 mg/L DPA, the contribution to TSN is the largest from the account of nitrogen nitrite and nitrogen nitrate. On the day 16th TSN has a maximum compared to the days 14th, 15th and 19th. In samples containing 3 and 6 mg/L NH_4^+ and 0.5mg/L of DPA, the contribution to TSN decreases at the excess of nitrite and especially of nitrate. The formation and oxidation dynamics of NO_2^- in the samples with 3 mg/L and 6 mg/L of NH_4^+ show several differences (Figs. 7 and 8).

Table2 Soluble mineral nitrogen in river water models within 14-19th days

Test time, days	NH ₄ ⁺ nitrogen, mg/L	NO ₂ ⁻ nitrogen, mg/L	NO ₃ ⁻ nitrogen, mg/L	Total nitrogen, mg/L
Initially 3mg/L NH ₄ and 0.05 DPA				
14	1.37	0.197	2.43	4.00
15	1.34	0.880	1.52	3.74
16	2.32	0.457	1.93	4.71
19	0.68	1.040	1.77	3.49
Initially 6mg/L NH ₄ and 0.05mg/L DPA				
14	1.490	1.185	4.62	7.29
15	1.030	1.257	0.70	2.99
16	0.820	2.459	7.47	10.75
19	0.120	2.824	9.67	12.61
Initially 3mg/L NH ₄ and 0.5mg/L DPA				
14	1.420	0.571	1.99	3.98
15	1.420	0.274	2.92	4.61
16	1.030	1.129	3.29	5.44
19	0.930	1.617	4.38	6.93
Initially 6mg/L NH ₄ and 0.5 mg/L DPA				
14	2.340	0.317	4.45	7.11
15	1.800	1.074	7.39	10.16
16	1.090	2.445	8.48	12.01
19	0.310	2.671	8.56	11.54

However, it can also be assumed some similarity of the dynamics in nitrite ion concentrations for these samples. Comparing the influence of 1-NA and DPA concentrations on nitrogen species mechanism in natural waters, one can conclude that the impact of the presence of 1-NA in natural waters is much higher. This is connected to the environmental safety and the requirement to develop new methods of decomposition, degradation/biodegradation of ammonium derivatives, containing benzene ring and naphthylamines (Baneshi et al.2017, Börnick et al. 2001, Norzaee et al. 2017, Paździor et al.2009, Babcock et al. 1993, Shin and Spain 2009). Unfortunately, even if there are numerous methods developed

for aniline and diphenylamine with a satisfactory result, the existing methods for 1-NA are scarce, with an uncertain efficiency.

Conclusion

Natural water model experiments show that ammonium derivatives have a brake impact on redox processes of stable soluble nitrogen forms at concentrations below MAC. By increasing their concentration in river waters, the effect becomes more obvious. By laboratory simulations, two types of fixations by microbial organisms have been distinguished: 1) Ammonium absorption-desorption, e.g. HMBRA, at the instantaneous increase in the NH_4^+ concentration in the river waters (so-called shock/stress effect); 2) Nitrogen fixation stimulated by a certain concentration (0.05mg/L) of 1-NA and other analyzed amines. These modifications constitute a sensitive reaction of aquatic microorganisms to environmental changes. A noticeable effect of the attenuation of nitrification processes caused by the toxicity of ammonium derivatives has been evidenced. All at once, the models with diethylamine reveal an increase in NH_4^+ concentration due to its decomposition (approx. 3.5–3.8 mg/L nitrogen of NH_4^+). Slightly degradable organic carbon influences the transformation of nitrogen species into ammonia, leading to a decrease in nitrite concentrations over a sufficiently long period of time. Diethylamine, being easily degradable, causes an increase in the concentration of ammonium ions due to the transformation of its amino nitrogen and the reduction of nitrites and nitrates through its organic carbon.

Abbreviations

SAS-Ct/An: cationic/anionic surfactants (surface-active substances); 1-NA: 1-naphthylamine; DEA: diethylamine; DNRA: type of dissimilatory nitrate reduction to ammonium; DPA: diphenylamine; MAC: Maximum Allowable Concentration; HMBRA: hydromicrobiotic reaction to ammonium; TSN: total soluble nitrogen.

Declarations

Acknowledgment

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Authors' contributions

PS is the only author of this manuscript. PS has designed the study, collected data, carried out fieldwork and experiments and interpreted the results of the manuscript. PS has contributed to whole bibliographic, reviewing, and editorial works.

Availability of data and materials

All data are included in the manuscript.

Ethics approval and consent to participate

Not applicable.

Consent for publication

I agreed to publication in the Scientific Reports journal.

Competing interests

The author declares that he has no competing interests.

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Figures

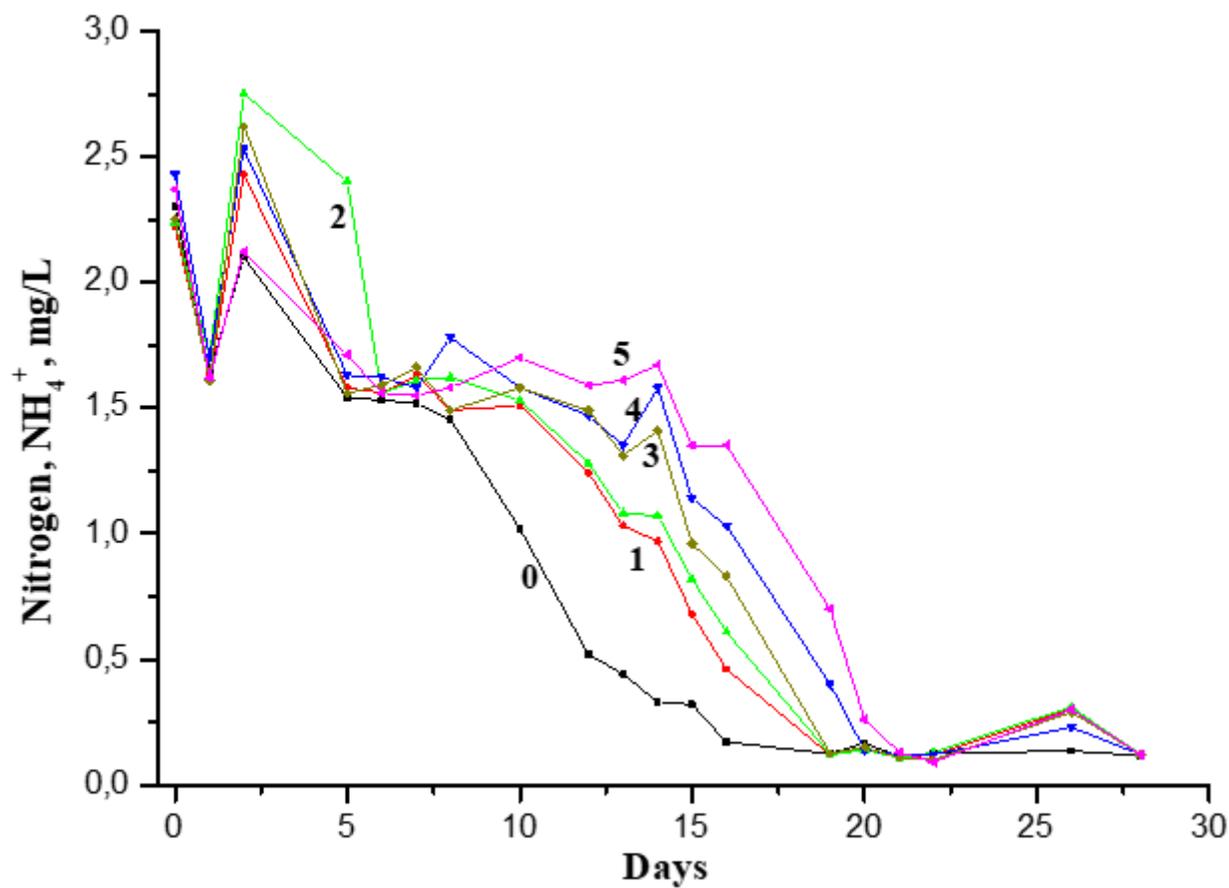


Figure 1

Dynamics of ammonium ions concentration in the Nistru River water containing 3 mg/L NH_4^+ in the presence of 1-naphthylamine: 0) 0 mg/L, reference sample; 1) 0.025 mg/L (0.5 MAC); 2) 0.05 mg/L (1.0 MAC); 3) 0.1 mg/L (2.0 MAC); 4) 0.25 mg/L (5 MAC); 5) 0.5 mg/L (10 MAC).

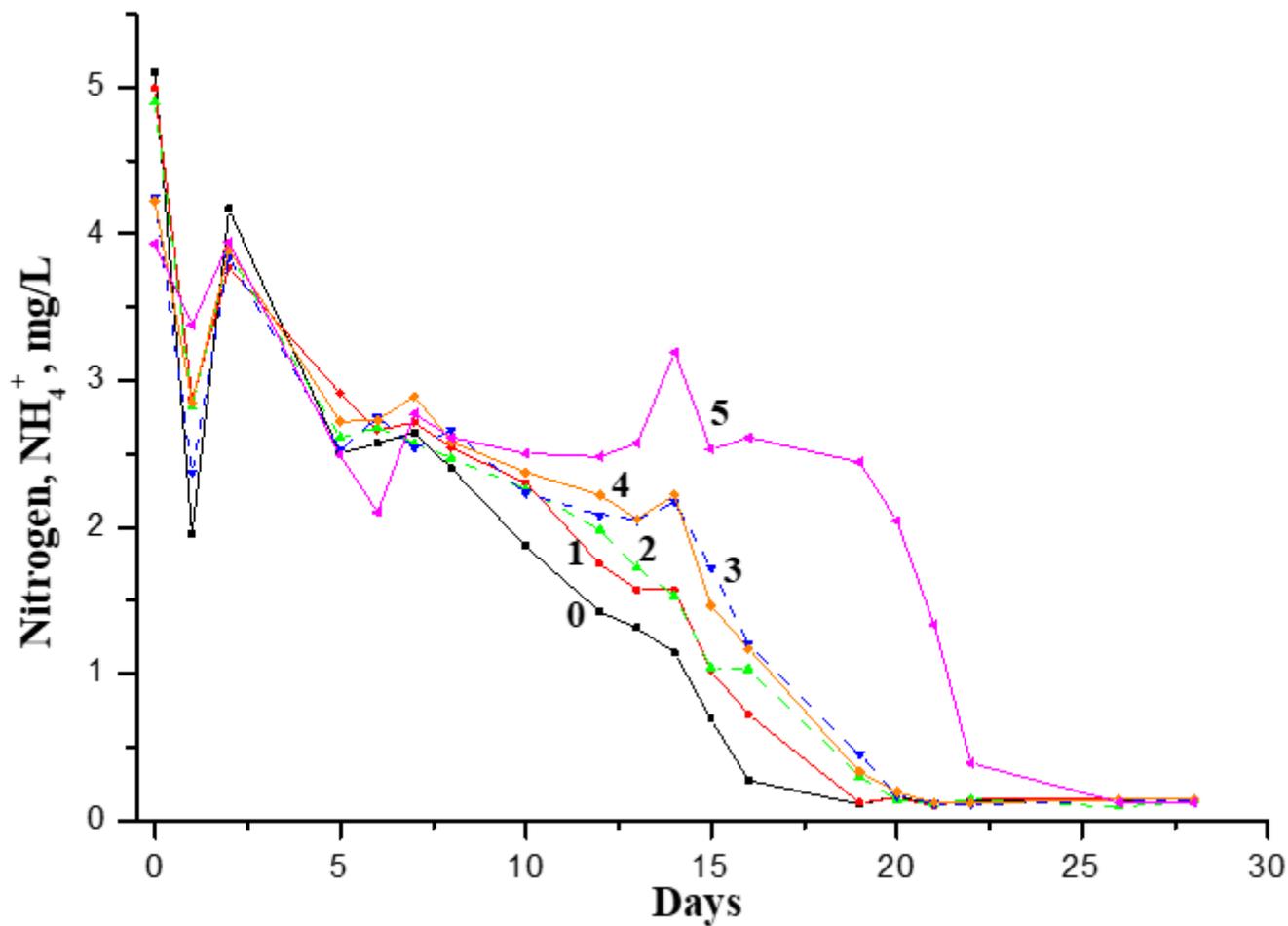


Figure 2

Dynamics of ammonium ions concentration in the Nistru River water containing 6 mg/L NH_4^+ in the presence of 1-naphthylamine: 0) 0 mg/L, reference sample; 1) 0.025 mg/L (0.5 MAC); 2) 0.05 mg/L (1.0 MAC); 3) 0.1 mg/L (2.0 MAC); 4) 0.25 mg/L (5 MAC); 5) 0.5 mg/L (10 MAC).

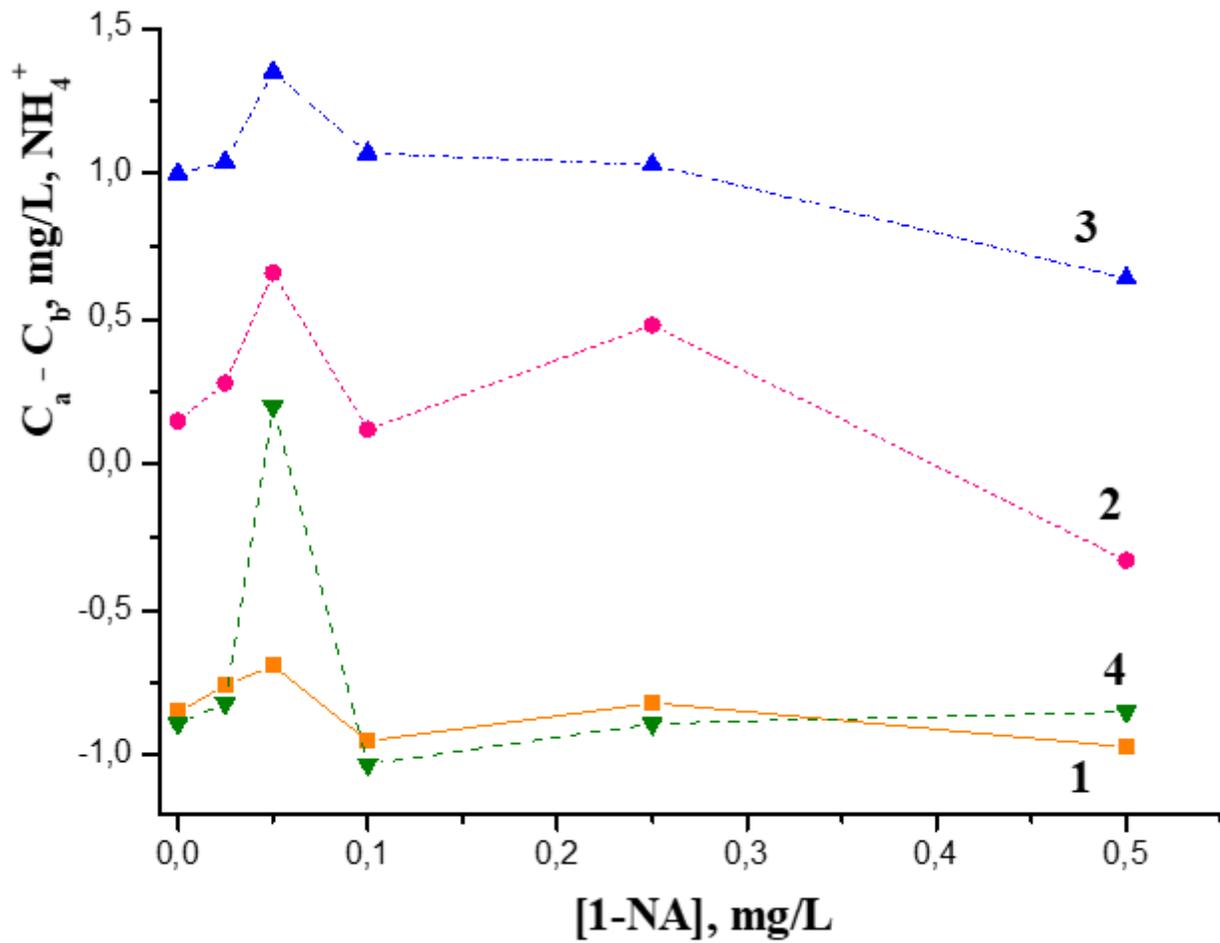


Figure 3

The difference of ammonium ion concentrations: 1) (C1-C0); 2) (C2-C0); 3) (C2-C1); 4) (C3-C0) in function of 1-NA concentration with initial 3 mg/L NH₄⁺.

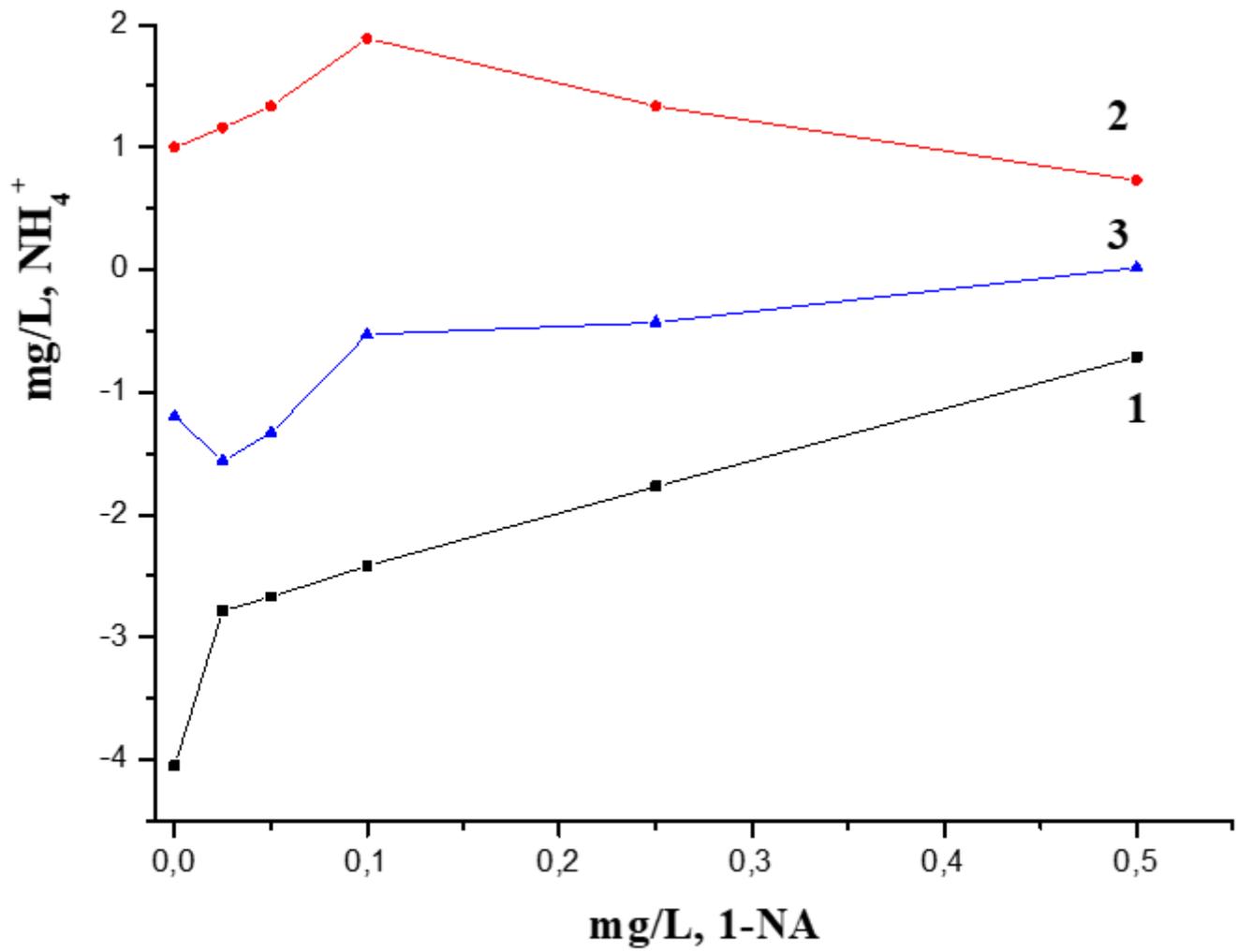


Figure 4

The difference of ammonium ion concentrations: 1) (C1-C0); 2) (C2-C1); 3) (C2-C0) in function of 1-NA concentration in the laboratory simulations with initial 6 mg/L NH₄⁺.

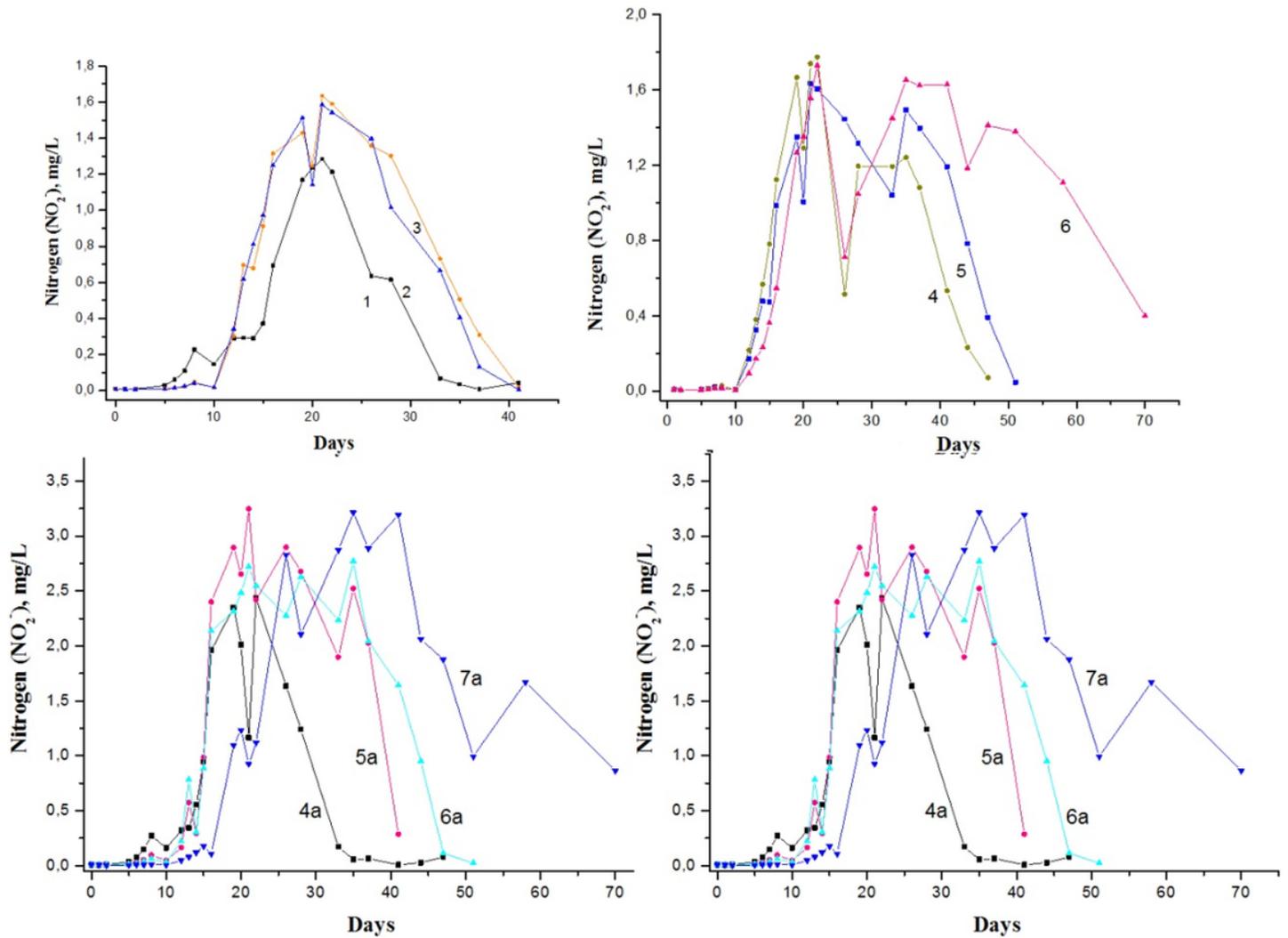


Figure 5

Dynamics of the nitrite ions concentration in the Nistru River water (Vadul-lui-Voda section), containing: 3 mg/L NH_4^+ (plots from above) (1- the reference sample, 2- with 0.025 mg/L 1-NA, 3- with 0.05 mg/L 1-NA, 4 – with 0.1 mg/L 1-NA, 5- with 0.25 mg/L 1-NA, 6- with 0.5 mg/L 1-NA) and 6 mg/L NH_4^+ (plots from the bottom) (1a and 4a - the reference sample, 2a – with 0.025 mg/L 1-NA, 3a - with 0.05 mg/L 1-NA, 5a – with 0.1 mg/L 1-NA, 6a – with 0.25 mg/L 1-NA, 7a - with 0.5 mg/L of 1-naphtylamine) initially.

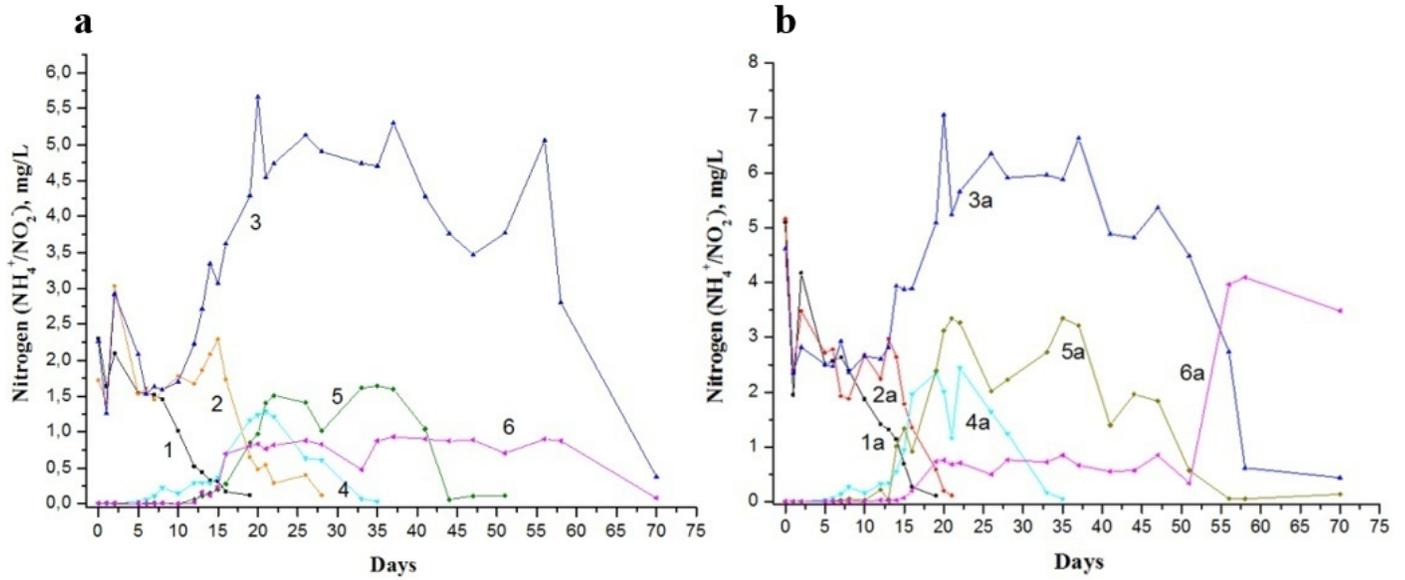


Figure 6

a. Dynamics of the ammonium ion concentration (1- the reference sample, 2- with 2.0 mg/L, 3- with 20.0 mg/L DEA) and nitrite concentration (4- the reference sample, 5- with 2.0 mg/L, 6- with 20.0 mg/L DEA) in the Nistru River water (Vadul-lui-Voda section) with 3 mg/L NH_4^+ initially. b. Dynamics of the ammonium ion concentration (1a- the reference sample, 2a- with 2.0 mg/L, 3a- with 20.0 mg/L DEA) and nitrite concentration (4a- the reference sample, 5a- with 2.0 mg/L, 6a- with 20.0 mg/L DEA) in the Nistru River water (Vadul-lui-Voda section) with 6 mg/L NH_4^+ initially.

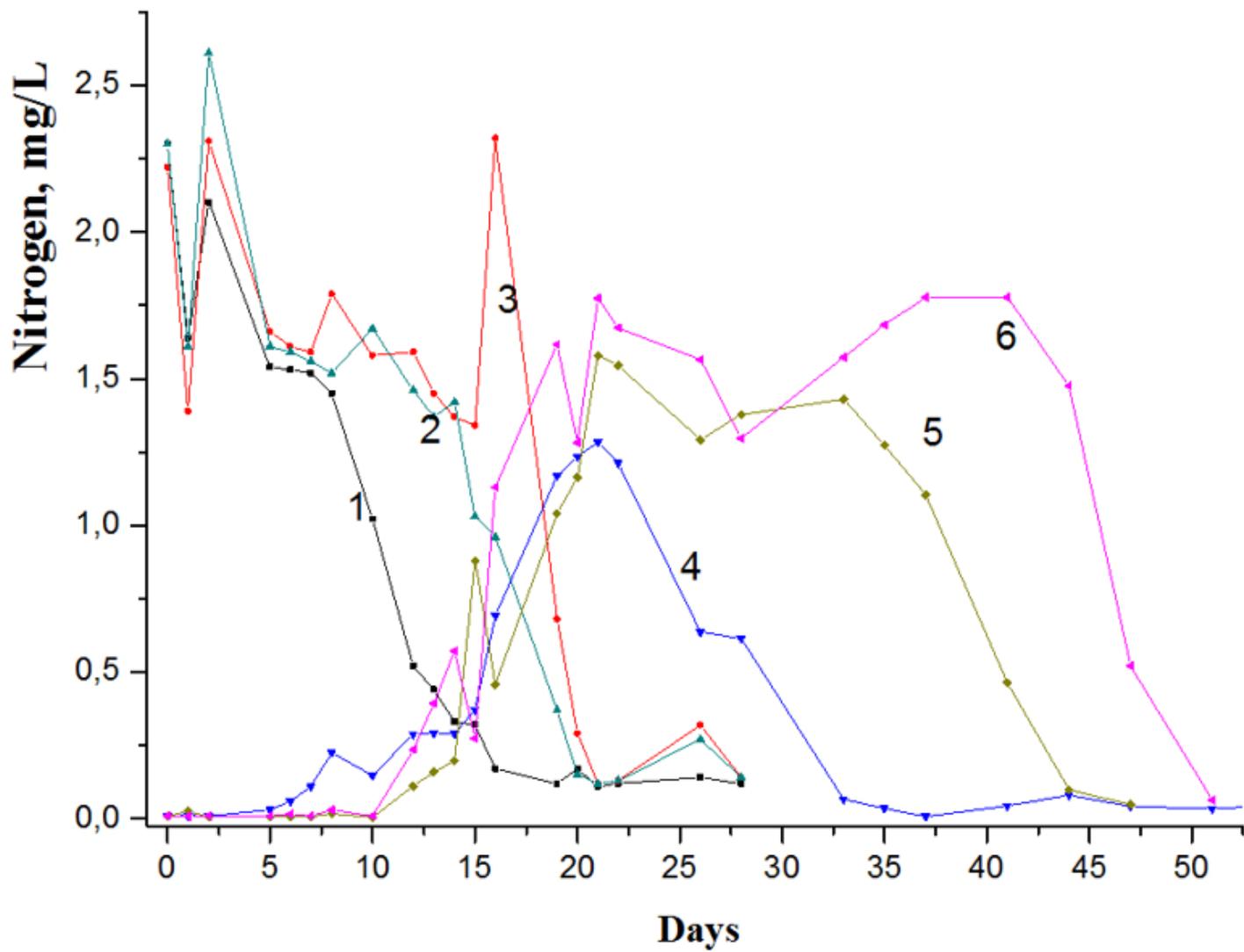


Figure 7

The dynamics of ammonium (1- reference sample, 2- with 0.5 mg/L, 3- with 0.05 mg/L of diphenylamine) and nitrite ions (4- reference sample, 5- with 0.05 mg/L, 6- with 0.5 mg/L, of diphenylamine) in model samples with 3 mg/L NH_4^+ in the Nistru River water.

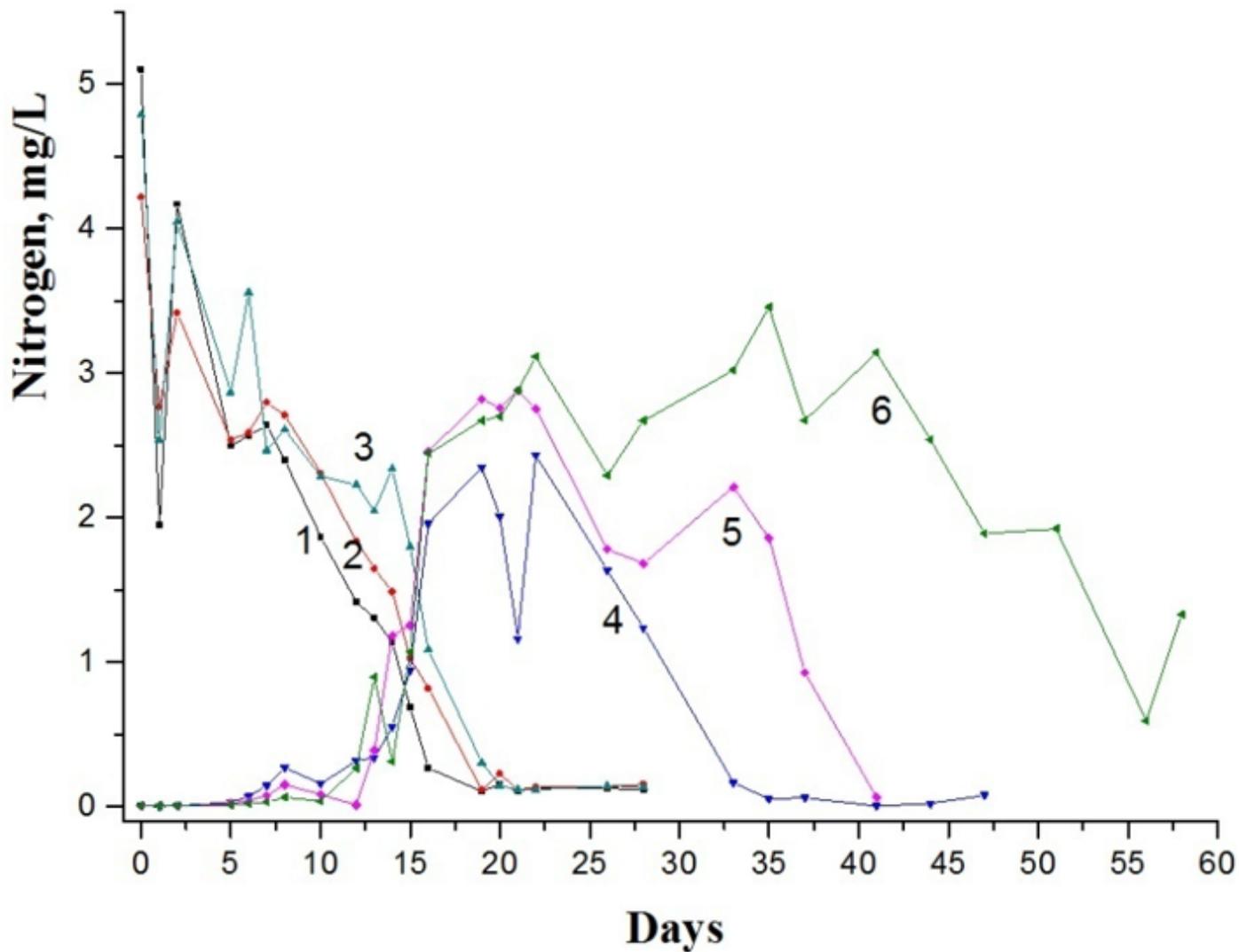


Figure 8

The dynamics of ammonium (1- reference sample, 2- with 0.05 mg/L, 3- with 0.5 mg/L of diphenylamine) and nitrite ions (4- reference sample, 5- with 0.05 mg/L, 6- with 0.5 mg/L of diphenylamine) in model samples with 6 mg/L NH_4^+ in the Nistru River water.