

THE EVOLUTION OF BIOCHEMICAL OXIDATION OF AMMONIA IONS IN SMALL RIVERS WATER

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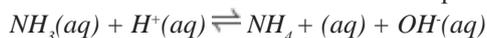
Abstract: Nitrification is the oxidation of ammonia to nitrate, via nitrite and it occupies a central position within the global nitrogen cycle. Nitrifying bacteria are the organisms capable of converting the most reduced form of nitrogen, ammonia, to the most oxidised form, nitrate, but their activity is influenced by pollution level. Starting with the assumption that pollution of small internal water courses in the Republic of Moldova remained severe (phenols, detergents and copper regularly exceed the MACs) the work presented in the paper discusses the evolution of ammonia ions nitrification in the water of river Prut tributaries and its correlation with the content of pollutants in water: surface-active substances, Cu, BOD₅, COD and other compounds.

Keywords: biochemical oxidation, ammonia ions, nitrification, small rivers.

Introduction

Ammonia is produced by human activity. It occurs naturally from the breakdown of nitrogenous organic compounds in water, soil and the breakdown of biota, being an important source of nitrogen which is needed by plants and animals.

The presence of ammonium ions in natural waters is associated with pollution caused by livestock, intensive agriculture, and liberation of domestic sewage in courses of superficial waters. A statistically significant increase in ammonium concentration was detected in pond water exposed to artificial radiation resembling sunlight in the UV range of the highest absorbance after 5 h of irradiation. In sea and river water a corresponding increase (< 0.5 μM) was recorded after an exposure time of 25 hours [1]. Trace amounts of ammonia (NH₃) in unpolluted water are present from the reduction of atmospheric nitrogen by aquatic microorganisms. Ammonia is at equilibrium with ammonium ion (NH₄⁺) and the equilibrium reaction between ammonia and ammonium ion is pH dependent.

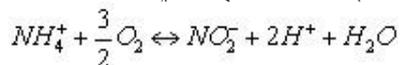


So Thus, total ammonia is the sum of the two forms. Natural unpolluted waters may contain 0 to 3 mg/l. Higher concentrations correspond to pollution and can be toxic to aquatic organisms. Sources of ammonia may be industrial discharges, particularly from the pulp and paper industry, fertilizer runoff, sewage releases into natural waters, and industrial releases.

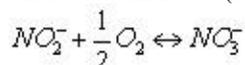
Ammonia and ammonium salts are also found in small quantities in rainwater (ammonium chloride, sulfate and bicarbonate).

The plants (usually through their roots) consume ammonia taken up directly. Most of the ammonia is converted as a result of biochemical oxidation from a reduced to a more oxidized state, nitrate, by the Nitrifying bacteria. This is accomplished in two steps:

- Bacteria of the genus **Nitrosomonas** oxidize NH₄⁺/NH₃ to **nitrites** (NO₂⁻).



- Bacteria of the genus **Nitrobacter** oxidize nitrites to **nitrates** (NO₃⁻).



The oxidation of ammonia to nitrate by microorganisms is a key process in the nitrogen cycle, resulting in nitrogen loss from ecosystems, eutrophication of surface and ground waters. In aquatic ecosystems nitrifiers compete with primary producers for ammonia and in all ecosystems nitrification results in the generation of reactive gases, in particular nitrous oxide, involved in the destruction of stratospheric ozone and global warming.

Effluents containing nitrogenous compounds must be treated in order to reduce the release of ammonium-N into natural waters, because this causes oxygen demand, is toxic to aquatic life, leads to eutrophication, modifying the biota and creating an ecological imbalance.

The First Step of the process ($\text{NH}_4^+ \rightarrow \text{NO}_2^-$; 66 kcal of energy are liberated per gram atom of ammonia oxidized) involved microorganisms called the ammonia oxidizers. The biochemical nitrite Oxidation ($\text{NO}_2^- + 1/2 \text{O}_2 \rightarrow \text{NO}_3^-$; 18 kcal of energy is liberated per gram atom of nitrite oxidized) is the second step. Nitrate is the final product after completion of the biochemical oxidation. Nitrifying bacteria work either at full capacity or drift into a resting phase. Some substances will influence bacteria activity, such as phenol, surface-active compounds, heavy metals and others [2-8].

The nitrification process can have a direct impact on water quality. The end result of nitrification, nitrate (NO_3^-), is a form of nitrogen that is highly mobile and easily moves with water. When rainfall is heavy, nitrates can move downward in the soil and then in underground waters.

Start with the assumption that pollution of small internal water courses in the Republic of Moldova remained severe, recorded concentrations of ammonium, nitrite and other pollutants (BOD_5 , oil products, phenols, and detergents) exceeded the maximum admissible concentration (MAC), the evolution of biochemical oxidation of ammonia ions in small rivers water was evaluated in this work.

To surface waters loads of pollution contributes the runoff from residential and industrial areas, domestic wastewater discharges from non-sewered population. The animal waste is not anymore concentrated in a limited number of sites; it is spread everywhere, on both private and public lands, threatening the drinking water sources and the surface waters. This major pollution source became more diffuse and less manageable. Another source of surface waters pollution is the non-observance of protection strips along the water courses. Within the settlements, these are transformed into domestic waste dumps.

Materials and Methods

It was used a combination of laboratory and field studies was used to elucidate the factors controlling the growth, activity and survival of nitrifiers in natural waters.

Nitrification capacity of small rivers water was investigated by means of laboratory modelling with employment of natural waters [9]. Analytical settlement of the problem was realized by controlling NH_4^+ , NO_2^- , NO_3^- , O_2 and pH.

In small rivers water, were determined the concentrations of macro-, nitrogen and organic compounds. Samples (3 000 ml) of different aquatic environments were enriched with $(\text{NH}_4)_2\text{SO}_4$ to concentrations of 2.0 – 6.0 mg/dm³ and incubated on natural conditions at 20-22°C. The content of NH_4^+ , NO_2^- and NO_3^- , and the pH were determined after the liquid was filtrated. This replacement procedure was repeated every 2-5 days.

Ammonia ions were determined by using the Nessler reactive [10]. Nitrite was estimated by the procedure with the Griess reagent, and the reduction method with the Zn-MnSO₄ mixture [11] was used to measure nitrate [12] and other compounds [13-16].

Results and discursions

The nitrification process can have a direct impact on water quality. The end result of nitrification, nitrate (NO_3^-), is a form of nitrogen that is highly mobile and easily moves with water. When rainfall is heavy, nitrates can move downward in the soil.

The river network in the Republic of Moldova is the final receptor of most runoff and wastewater, either household or industrial, as in any other country; the treatment level of wastewaters is insufficient and about 1/3 of pollutants, including ammonia compounds, pesticides, detergents, some heavy metals still persist after treatment, being discharged into natural waters. The concentrations of ammonium, nitrites, phenols, detergents and copper regularly exceed the MACs. For example, ammonium concentrations were found of 17,0 mg/dm³ as N (43,6 MAC) up to 46,5 mg/dm³ as N (119 MAC) in the Bic river, downstream Chisinau (wastewater treatment station, WWTS), maintaining their high values up to the confluence with the Nistru river [17].

Out by experimental obtained results it was established that $\text{NH}_4^+ \rightarrow \text{NO}_2^-$ process in modeling of small rivers Ciuhur, Larga, Draghiste, Lopatnic, Calanjir, Racovat, Vilia, Bogda, Camenca water it takes place in the same way as river Nistru water and lasts 6-10 days, whereas in river Racovat water, only 40-77% of ammonium ions are oxidizes. Even after 15-20 days, 7-20% of NH_4^+ remained in solutions. $\text{NH}_4^+ \rightarrow \text{NO}_2^-$ transformation in model with Vilia, Lopatnic (Lopatnic), Racovat (Grajdiesti) water take place in 15 days. In rivers Draghiste (Burlanesti), Bogda, Garla Mica, Bac, Racovat (Hadarauti), Raut (downstream Balti, Floresti, Orhei) and Cainari, the process lasts about 20-21 days, but in the case of r. Racovat (Clocusna), Lopatnic (Gremencauti), Draghiste (Bulboaca), Larga samples - 25 and more days (fig. 1, a-f). Process takes place for 21-25 days in the waters of r. Cainar (Gura Cainari), Ichel (Ratus), Isnovat (Ialoveni) and Camenca (Gura Camenca).

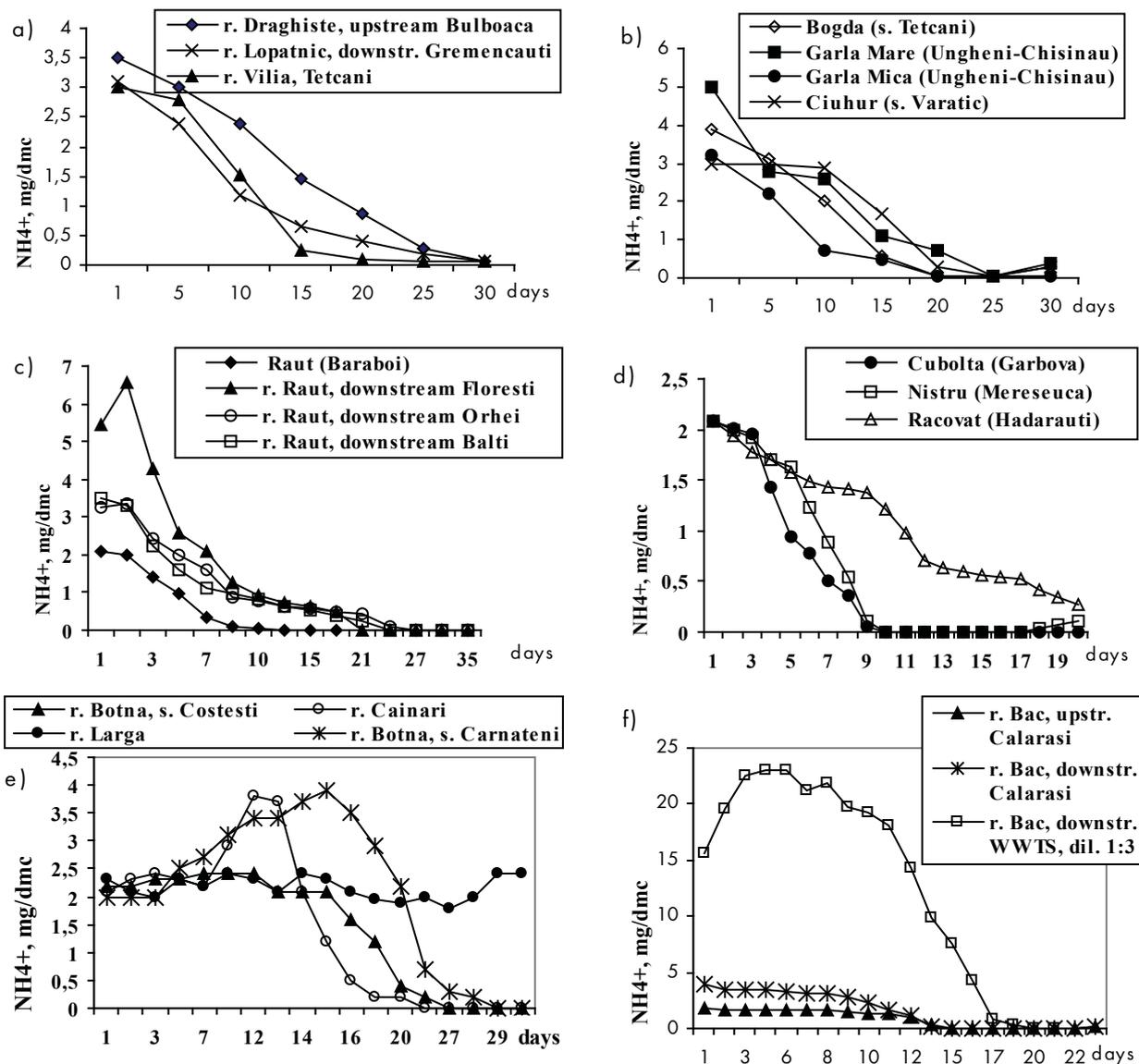
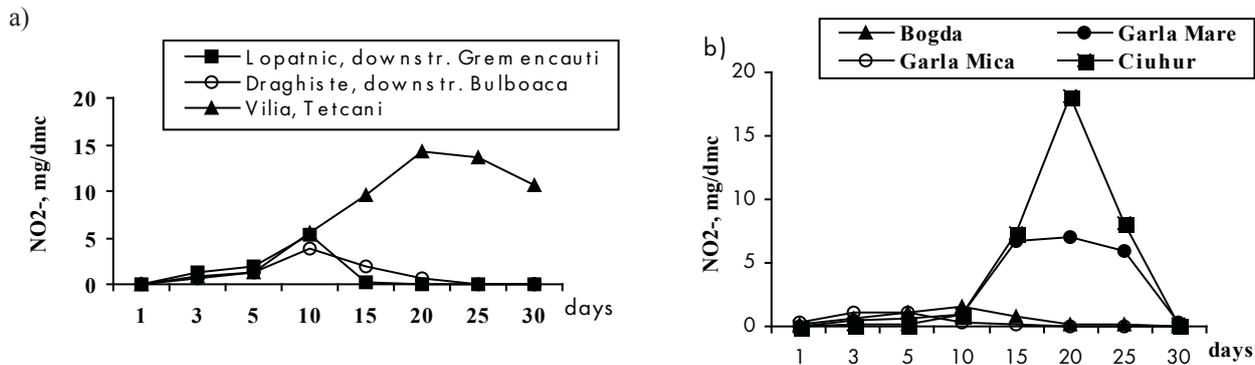


Figure 1. Evolution of $\text{NH}_4^+ \rightarrow \text{NO}_2^-$ process in small rivers water.

The second stage of nitrification ($\text{NO}_2^- \rightarrow \text{NO}_3^-$) lasts 15 days in Garla Mica, Lopatnic (Lopatnic), Racovaț (Grajdiesti) rivers water; in r. Draghiste, Lopatnic (Gremencauti), r. Vilia (Cotiugeni) and Bogda – 25 days; r. Racovat (Clocusna), r. Draghiste (Burlanesti), r. Vilia (Tetcani) and r. Ciuhur (Varatic) the transformation $\text{NO}_2^- \rightarrow \text{NO}_3^-$ was developed during 30 and more days. The time of nitrification correlates with the content of pollutants in water: surface-active substances, Cu, BOD_5 , COD and other compounds.



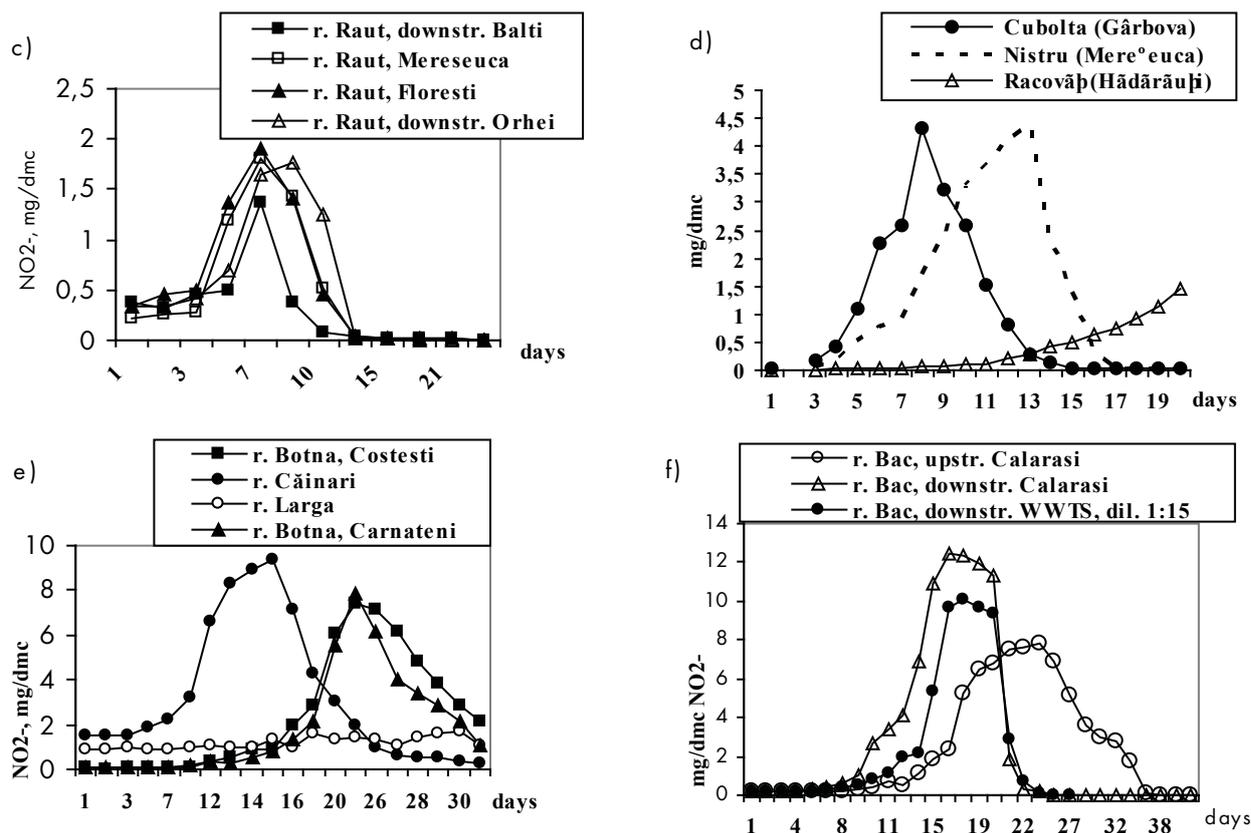


Figure 2. Evolution of the second stage of nitrification ($\text{NO}_2^- \rightarrow \text{NO}_3^-$) in rivers water.

The rate of ammonia oxidation exceeded the similar of nitrite process. Differences in oxidation rates can be attributed to ammonia-oxidizing bacteria out competing nitrite-oxidizing bacteria due to a number of factors, including free ammonia inhibition, dissolved oxygen concentration, heavy metals, organic matter, temperature and pH [18-20].

The study of nitrification in natural waters with high suspended-solid (SS) content indicated that the presence of SS could accelerate the nitrification process. The nitrification rate would increase non-linearly with the increase of suspended-solid content [21].

High suspended-solid content has useful implications for nitrogen removal from river systems in the Republic of Moldova: rivers Raut, Lopatnic, Cubolta, Cainari, Bac.

The time passing on ammonia ions oxidation is conditioned in natural small rivers water by organic and inorganic pollutants content, which influenced the activity of Nitrifying microorganisms, and correlated (fig. 2) with biological (BOD) and chemical oxygen demand (COD-Mn, COD-Cr).

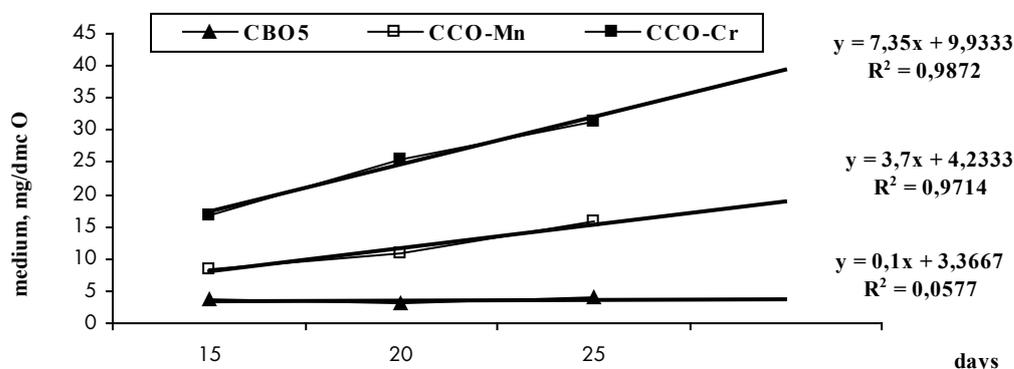


Figure 3. The correlation between the time of ammonia biochemical oxidation and BOD, COD-Mn and COD-Cr.

It is noticed that the improvement of natural waters state (quality, self purification, nitrification) depends on the implementation of water protection measures as soon as possible.

Conclusions:

1. Effluents containing nitrogenous compounds must be treated in order to reduce the release of ammonium-N into natural waters, because this causes oxygen demand, is toxic to aquatic life, leads to eutrophication, modifying the biota and creating an ecological imbalance.
2. The concentrations of ammonium regularly exceed the MACs (17,0 - 46,5 mg/dm³ as N, 43,6-119 MACs, in Bac river, downstream Chisinau, maintaining their high values up to the confluence with the Nistru river).
3. $\text{NH}_4^+ \rightarrow \text{NO}_2^-$ process in modeling of small rivers lasts from 6-10 till 21-25 days in dependence of pollutants content.
4. The second stage of nitrification ($\text{NO}_2^- \rightarrow \text{NO}_3^-$) lasts 15 - 30 and more days.
5. The time of nitrification correlates with the content of pollutants in water: BOD₅, COD and other indicators.
6. High suspended-solid content has useful implications for nitrogen removal from Raut, Lopatnic, Cubolta, Cainari, Bac river systems.

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