Environmental Engineering and Management Journal July 2018, Vol.17, No. 7, 1711-1719
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

STUDY OF NITROGEN FORMS IN SEASONAL DYNAMICS AND KINETICS OF NITRIFICATION AND DENITRIFICATION IN PRUT AND NISTRU RIVER WATERS

Petru Spataru[1], Igor Povar[1], Tudor Lupascu[1*], Alfredo Carlos Alder[2], Elena Mosanu[1]

[1]Institute of Chemistry, Academy of Sciences of Moldova, 3 Academiei str., Chisinau, MD2028, Republic of Moldova
[2]Eawag, Environmental Chemistry, Eawag, Environmental Chemistry, 133 Uberlandstrasse str., P.O. Box 611, Dubendorf, CH-8600, Switzerland

Abstract

The presence of nitrogen in its reduced forms serves as an indicator of natural aquatic system degradation. The excessive concentrations of nitrogen in reduced forms (NH_4^+, NO_2^-) found in the sections of the the Shireutsi (of the Prut River) and the Olaneshti (of the Nistru River) prove that these sites are areas to focus efforts on improving water quality. Laboratory simulations indicate a good environmental buffer action of natural waters to potential pollution in Sculeni and Ungheni sections of the Prut River and downstream of Naslavcea and Tiraspol (Nistru River), as well as in sites most affected by pollution with wastewater from Frasineshti (of the Prut River) along with Lencautsi, Cosautsi and downstream of Bender (the Nistru River). Overcoming the maximum allowable concentration (MAC) level for the nitrate ion in water from wells is an index of pollution of the land areas where pollutants can leach into and pollute groundwater. Of the 12 wells from which water samples were collected over three years (2010-2012), only two wells, in the Cuhneshti and Cobani villages showed MAC level compatible with drinking water quality.

Key words: Moldovan rivers, nitrogen forms, organic compounds, oxidation, seasonal dynamics

Received: January, 2013; Revised final: October, 2014; Accepted: October, 2014; Published in final edited form: July, 2018

1. Introduction

The issue of water as a whole, and specifically for drinking water in the Republic of Moldova is extremely important due to the phenomenon of aridity, which has become more and more pronounced over the last 5-7 years, from which one or two are usually dried. In the most part of the country the average return period of drought varies from 3 to 5 years. For the period spanning from 2000 to 2012 the Republic of Moldova has already experienced 4 years (2000, 2003, 2007, and 2012) with the devastating droughts (Cazac, et al., 2014). In the southern part of the country a significant number of small rivers in the summer period remains without water and only a few reservoirs are used.

The high pollution of wells is another huge concern, taking into account that wells are used as a source of water supply for about 75% of the rural population. Due to the increase in human activity, intensive agriculture, especially in the livestock sector, and the lack of ecological management, the water quality of wells does not correspond to the standards of "Drinking Water". This also regards the water from the distribution systems throughout the country. The ratio of the samples that exceeded the sanitary-chemical parameters from the underground centralized sources was 70.8% in 2009 and 67.8% in 2010. The most severe situation was recorded in the districts of Anenii Noi, Faleshti, Glodeni, Hinceshti, Causheni, Ciadyr-Lunga, Cimishlia, Comrat, Drochia, Sangerey and the Baltsy municipality where this index

* Author to whom all correspondence should be addressed: e-mail: lupascut@gmail.com; Phone: +37322739736; Fax: +37322739736

was between 85-100%. The absence of waste disposal systems as well as basic measures of water sources protection are the main causes of water quality worsening in wells. The ratio of wells that exceeded the sanitary-chemical parameters constituted 84.2% in 2010 (80.7% in 2009) (NRSERM, 2011).

The rivers Nistru and Prut are the largest in the Republic of Moldova and their basins comprise the entire territory of the country, form and store the most significant amounts of water. The waters of Nistru and Prut rivers meet the regulatory requirements for "Drinking Water" main mineral parameters and represent the greatest source of water for water treatment plants. The quality of water in these rivers is guaranteed mainly by self-purification processes that take place in water ecosystems.

Nitrogen, being one of the basic elements in the formation of organic substances, is among the most sensitive elements to change in the natural water due to eutrophication and pollution. The drinking water MAC level is for NH_4^+ 0.39 mg/L and NO_2^- - 0.02 mg/L (CD, 1998; State Register, 2007). The study of nitrogen mineral forms highlights the sustainability, as well as the vulnerability of the aquatic environment. Studies of the hydrochemistry and quality of the water of these rivers have been published in national specialized journals (Gladchi et al., 2008; Zubcov et al., 2011). Findings show that, for a wide range of bacteria, in contrast to the situation in animal (Martinelle et al., 1993) and plant cells (Britto et al., 2001, Britto et al., 2002), ammonia is not toxic, even in molar concentrations. This happens because most bacteria prefer ammonia as a nitrogen source; some species even produce ammonium ion – for example, N_2-fixing *Rhizobia Cyanobacteria* and *Proteolytic Clostridia* create ammonia through the fermentation of amino acids. Resistance to ammonia is a common property in terms of bacteria (Müller et al., 2006). However, nitrites are highly toxic to humans, flora and fauna, being an important concern regarding water quality. They implicate also in the pathology of gastric cancer (Brunning-Fann et al., 1993, Weng et al., 1992) and are a possible cause of migraines (Bradberry et al., 1994); they as well compromise the binding capacity of oxygen in the blood and may result in respiratory deficiencies of aquatic animals and humans (Blackall, 2000, Van Leeuwen, 2000). Understanding the toxicity of reduced forms of nitrogen requires the identification of methods of enhancing the oxidation of nitrification processes. Furthermore, the pollutants are frequently associated into ionogenic groups, becoming less active, and their toxicity decreases and the rate of oxidation/assimilation processes increase, respectively. Otherwise, if pollutants are not associated, their toxicity is higher and the processes of self-purification are blocked (Lewis, 1992).

It is well-known that in the case of nitrification and denitrification the nitrite ion is an intermediate product. Both processes, oxidation of ammonia (first stage of nitrification) and denitrification are generated by specific enzymes, which cause the production of the same intermediate product - nitrite ion (Philips et al., 2002). The nitrite ion concentration, as an indicator of oxidation processes generated by the enzymatic catalysis, is higher than the MAC value in the abovementioned samples, as well as in such localities near the Prut River, as the town of Leova and the city of Cahul. In the composed sample from the Valea Mare section, this concentration is higher than the average value from the same section and period of time, which denotes its authenticity due to biochemical processes.

Consequently, the main goal of this paper was to study the nitrogen-containing species in function of seasons as well as kinetics of nitrification and de-nitrification in the Prut and Nistru waters.

2. Methods

Within the Scientific Co-oPeration between Eastern Europe and Switzerland (SCOPES) project (*see Acknowledgments*), during the 2010-2012 years, a large amount of aquatic samples were taken from different sections of the Prut and Nistru rivers (see the map, Fig.1), and analytical tests were carried out. Sampling on the Prut River was started from the border between the Republic of Moldova and Ukraine, above the lake dam (Criva and Shireuti, placed after the administrative centre Lipcani) and almost immediately after the lake (Branishte). The next sections were Sculeni and upstream Ungheni (32.5), before wastewater treatment plant (WWTP), which are less affected by human activity. Valea Mare is a section after the WWTP Ungheni. The Frasinesti section is downstream of the confluence with Jijia crossing the urban centres Dorohoi (24.3) and Vladeni and bringing through the Bahlui River polluted waters from Iassy (321.6). Cotul Morii is a less affected area, with reduced population. The Leova and Cahul cities have respectively 11.4 and 40.9 thousands inhabitants. The section Giurgiulesti is influenced by the Danube waters due to frequent changes of its water level. In this segment the Prut water is mixed with that of Danube. The sampling sites of the Nistru River were mostly chosen close to the towns and cities, as Soroca (28.6), Camenca (23.2), Ribnita (73.6) and Rezina (10.2) on its middle and Dubasari (35.2), Bender (99.3), Tiraspol (146.6) and Chisinau (804) on its bottom part.

The oxygen fixing and laboratory simulation initiating were started along with sampling processes. Under real conditions many investigations are impossible or extremely difficult to accomplish. At the same time, laboratory simulations offer the opportunity to study the process at the desired stage and analyze the degree of influence of a series of chemical and physicochemical parameters, as the concentration of different components, redox potential, temperature etc. Preliminary tests were made for the main mineral parameters: (Ca^{2+}, Mg^{2+}, NH_4^+, NO_2^-, NO_3^-, SO_4^{2+}, HCO_3^-, Cl^-), pH and dissolved oxygen, BOD_5, COO-Cr.

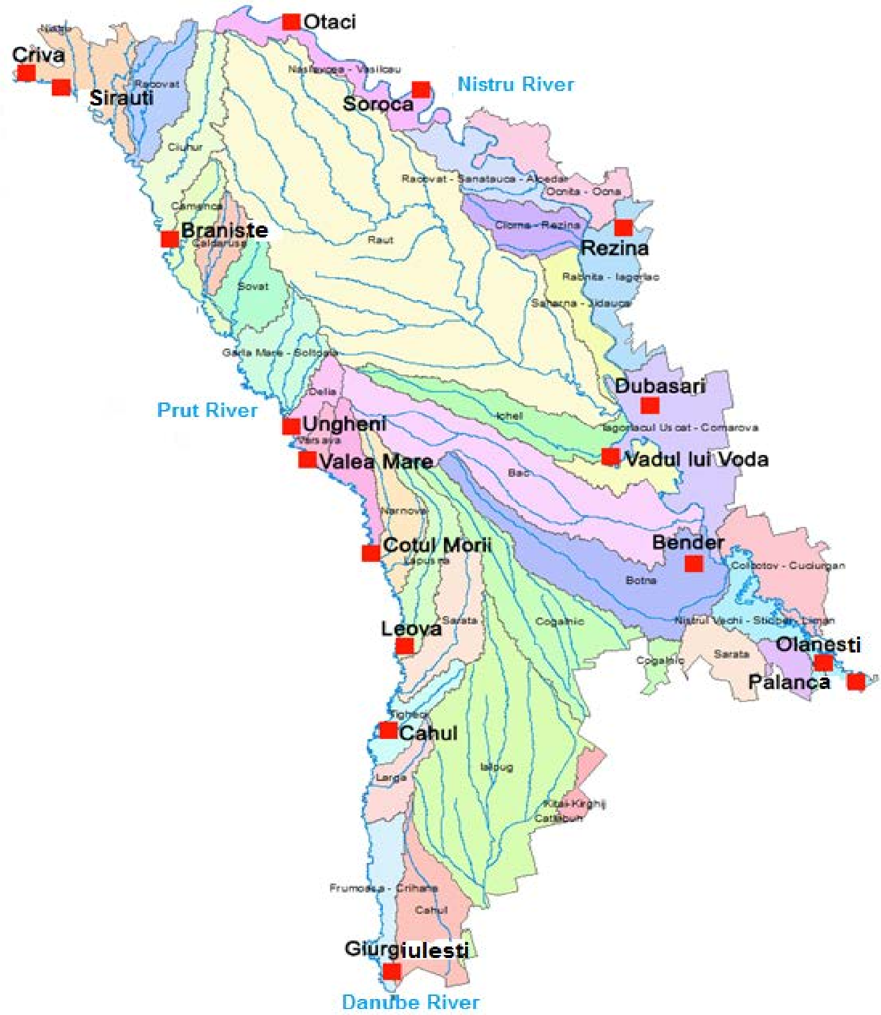


Fig.1. The map of the investigated sites, denoted by read squares

The natural water tests were carried out according to ISO methods (ISO 7150-1, 2001; SR ISO 7890-3, 1988; ISO 8466-1, 1990; SR ISO 7890-3, 2000; SR EN 26777, 2006; Sandu et al., 1989). Laboratory simultations were carried out respecting the minimum recommended of water amount for the tested sample in glass bottles (Matveeva et al., (1988). In each sample a solution of NH4Cl was added in order to obtain an initial concentration of 2 mg/L of ammonium. The tested water samples were kept in natural light conditions and spared from direct rays. Composed samples over a period of 20 days were also taken and studied. Test methods were carried out using HACH Company spectrophotometer (2004).

3. Results and discussion

3.1. Analysis of experimental data for the Prut River

In the first year of our studies (2010) ammonium ion concentrations that exceeded the MAC ("Drinking Water") were detected in some sampling sections. Ammonium produced by the decomposition of organic substances affects mostly small rivers. It also has an evident impact on the larger rivers.

For instance, the ammonium ion concentration in the spring water samples of the Camenca River (near the Balatina village) exceeded 2 MAC; for the Lapusna River (in the summer period) exceeded 1.1 MAC; for the Prut River (the Sculeni village) in summer, the Valea Mare village in summer and in the Leova town in fall overcome the MAC by 1.5, 1.4 and 1.2 times respectively.

The obtained results were compared with data obtained by the State Hydrometeorological Service, HydroMeteo (MB, 2011). The samples were collected monthly, so in total for each section in two years 24 samples were collected. The comparative analysis of data obtained by HydroMeteo and our laboratory simulations reveals the strength of natural waters to return to the required standard levels for drinking water and provides a deeper understanding about changes in the aquatic environment. The data on exceeded MAC values for ammonium and nitrite in the period of 2011-2012 yrs denote the changes that take place in considered cases in the course of the middle and bottom of the Prut River (Fig.2), that were reported by the State Hydrometeorological Service (MB, 2011).

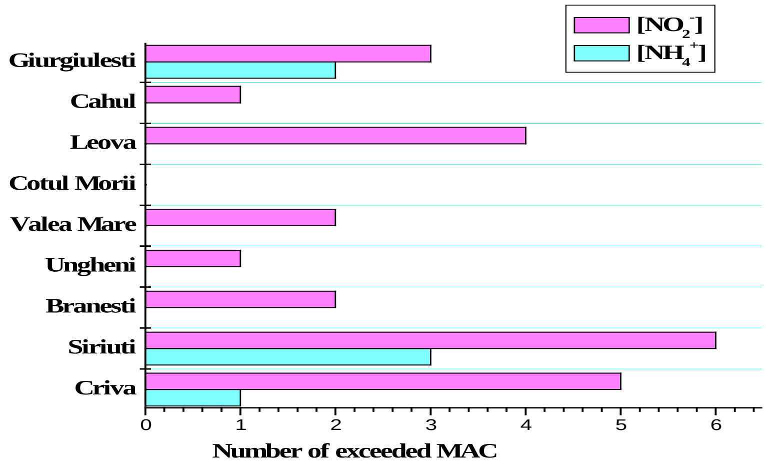


Fig. 2. The number of samples in which the concentrations of NH_4^+ and NO_2^- overcome the MAC values in the middle and bottom sections of the Prut River

Table 1. The concentrations of NH_4^+, NO_2^- and NO_3^- in samples taken from the middle and lower sections of the Prut River in 2011

Sampling site/month	***May***	***November***	***May***	***November***	***May***	***November***
Sections of the Prut River	***[NH4+], mgN/L MAC=0.39***		***[NO2-], mgN/L MAC=0.02***		***[NO3-], mg/L***	
village Sculeni		0.16		0.006		0.46
city Ungheni	0.38	0.2	0.018	0.009	1.5	0.48
village Macaresti	0.59		0.026		1.9	
village Valea Mare after the Jijia River		0.19		0.003		0.97
after the Leova town	0.48		0.026		1.95	
village Stoianovca	0.28		0.017		1.91	
village Branza after the Cahul city	0.55	0.13	0.063	0.007	1.88	0.86

Table 2. The concentrations of NH_4^+, NO_2^-, NO_3^-, O_2 and BOD_5 in samples taken from the middle and lower sections of the Prut River in 2012

Sampling site/concentration Sections of the Prut River	***[NH4+] mgN/L***	***[NO2] mgN/L***	***[NO3-] mg/L***	***BOD5 mgO/L (NO2-)***	***[O2] mg/L***
village Suleni	0.14	**0.038**	2.1	0.97(0.126)	9.53
city Ungeni after WWTP	0.21	**0.038**	3.2	0.82 (0.086)	9.41
village Valea Mare after Jijia	0.16	**0.038**	4.1	0.80(0.016)	9.09
After the Leova town	0.22	0.023	3.2	0.79(0.257)	9.11
village Branza after the Cahul city	0.3	**0.046**	2.9	0.86(0.211)	9.07

The dynamics of the accident cases (that exceeded the MAC values for NH_4^+ and NO_2^-) demonstrates an evident influence of anthropic impact on the aquatic environment, at the border with Ukraine in the North (up to Lake Costesti-Stanca) and the Branishte section, which is downstream of this reservoir. In the South (the Giurgiuleshti section), the water quality of the River Prut is impacted by the Danube River (Teodoru et al., 2007). The processes of assimilation and oxidation of organic matter are significantly more intense upstream of Lake Costesti - Stanca (the Criva and Shireuti sections) as well as in the Leova section; while in the Giurgiuleshti section they are less obvious. In other words, the more polluted is area, the less intense are the processes of assimilation and oxidation of organic matter.

The study of the nitrogen-containing species in waters of the Prut River in the years 2011-2012 highlights the values that exceed the MAC ("drinking water"), especially in the Branza village, which overran the MAC for the ammonium ion concentration in 2011, as well as for the nitrite ion in 2011 and 2012 yrs (Tables 1 and 2).

The most significant decompositions and oxidation of organic material in waters are more evident in the Prut River, especially in the Branza section downstream of the Cahul city.

3.2. Laboratory kinetic simulation for the Prut waters

Using the laboratory simulations, the water samples were studied from the following Prut River sections: the Sculeni village, the Ungheni city (downstream of WWTP), the Valea Mare village (downstream of the Jijia River), downstream of the Leova town and the Branza village. During a period of 8 to 13 days, the ammonia oxidation reached a level of about 2 mg/L (Fig. 3).

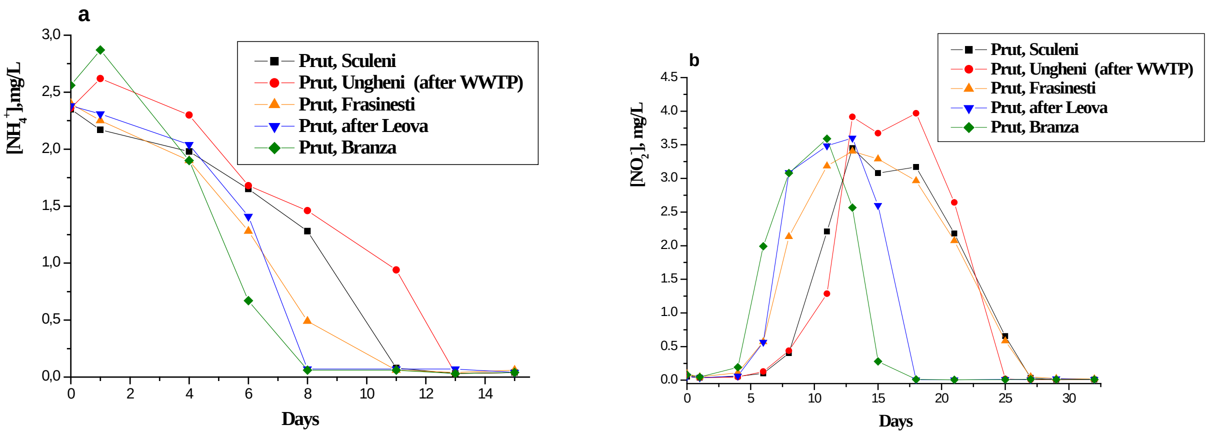


Fig. 3. The kinetics of the NH_4^+ (a) and NO_2^- (b) oxidation for the samples from the following Prut River sections: 1 – the Sculeni village, 2 – the Ungheni city (downstream of WWTP), 3 –the Valea Mare village (downstream of the Jijia River), 4 - downstream of the Leova town and 5 –the Branza village

The obtained data of inorganic forms of nitrogen are comparable to those of the Yangtze River in which there is a noticeable human impact (Muller et al., 2008) and are overcome by the eutrophic water of the Haihe River, from a semi-arid zone of China (Pernet-Coudrier et al., 2012). In sections of water downstream of Leova and Branza, the ammonia oxidation, assimilation of organic compounds, as well as undergoing transformations under the influence of natural enzymes produced by micro-organisms, proceeded very fast.

It is known that the numeric rising of heterotrophic populations in natural water (Daum et al., 1998) is coupled with the increase of nitrite concentration (Spataru, 2011; Lin et al., 2010). The samples least prepared for pollution are from the Sculeni and Ungheni sections. The full process of assimilation /oxidation of the reduced nitrogen and carbon forms for Frasineshti, however, is the longest, that according to the BOD_5 index and the concentration of nitrites in the destructible sample in the dark, demonstrates that water sample from the Prut - Valea Mare, along with the highest content of organic substance, containts xenobionts, that break the oxidation of carbon and reduced nitrogen forms. The complex compounds, which are the ammonia associated with a wide range of organic substances (humic complexes), can reduce the toxic effect of ammonia (for example, in the Leova and Branza samples). In the case of the water sample from the Prut – (Valea Mare section), the toxic effect of ammonia is diminished. Instead, a large amount of organic matter (in comparison with the rest of the samples) along with the presence of toxic pollutants causes a delay of purification processes (Philips et al., 2002).

3.3. Analysis of experimental data for the Nistru River

Fig. 4 illustrates that for the Nistru River the lowest values of these parameters for accidental cases (ammonium, nitrites) were recorded in the North, which was caused by the Novodnestrovsc Dam Lake, where the processes of sedimentation and sewage causing an "inertia" of indicators took place, at the same time as the Dam Lake Stanca-Costesti gave a stability of the nitrogen forms in the water of the Prut River. The water quality of the Nistru River is affected especially at the Olaneshti section, and to a lesser extent in the sections of Soroca, Dubasari, Vadul-lui-Voda and Bender. In the Bik River (tributary of Dniester), downstream of Chisinau, the ammonium concentration is found to be about 10-40 mg/L while at the confluence with the River Nistru ammonia exceeds 50mg/L. Formation of ammonium in wastewaters is mainly supposed to be due to the decomposition of organic matter from foodborne/ digestion products containing proteins and urea.

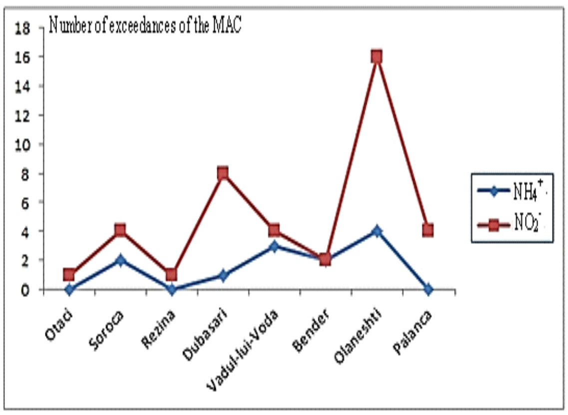


Fig. 4. The number of samples in which the concentrations of NH_4^+ and NO_2^- exceeded the MAC values in waters of the Nistru River

As one can see from Fig. 4, the anthropogenic accumulations lead to the increase of the exceeded MAC cases, that is a curve with peaks, which amplitude is growing to inferior sections, culminating in the Olaneshti one, and then returns to the normal shape up to the Palanca section.

A special case is the pollution of the Dubasari section. Upstream of this is the Rezina section (Fig. 4), where a minimum frequency of prevailing MAC was found for both ammonia and nitrites. Up to the Dubasari section, where many cases of the MAC overruns for nitrites have been found, there are not urban centers which would so strongly influence the aquatic environment. It appears that the impact on this segment is from the secondary pollution of lake sediments. The secondary pollution is called the pollution that takes place at the interface “water-sediment”, caused by underwater deposits, as pesticides and heavy metals (Linnik and Zubenko, 2000; Zubcov et al., 2010). The Lake Stanca-Costeshti is younger than Lake Dubasari, resulting in a lack of evident impact of the secondary pollution in the accumulation lake of the Prut River. Therefore, in this case the secondary pollution is a major factor that leads to the decrease of sustainability of the water treatment system on a segment of the Nistru River.

3.4. Laboratory kinetic simulations for the Prut waters

The laboratory kinetic simulation from 2011 demonstrates that in the sample, taken from the Naslavcea section, the oxidation process occurred most quickly (8 days). In the previous publication (Spataru, 2011) there were presented data on solved oxygen in this section that was lower than in the downstream sections, while the value of BOD_5 was higher in comparison with the same sections.

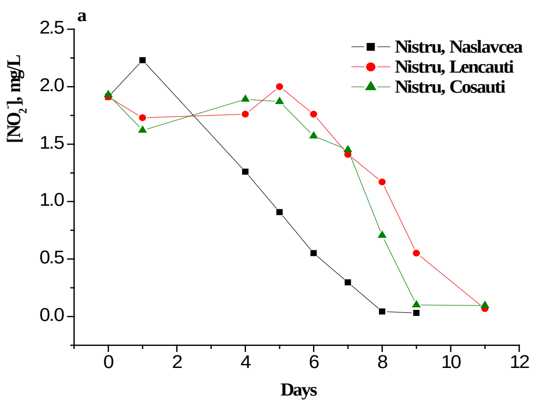
So, it is found that increasing the oxygen concentration has an opposite effect. This result can be explained by the following evidence. The value of BOD_5 in the Naslavcea village is higher in comparison with the values of this parameter in the downstream sections, since enzyme activity is greater. The oxidation of ammonia, nitrates and organic substances is related to the fact that the water spilled out of the lake dam comes from the depth zone of thermocline, where the activity of micro-organisms and biochemical activity is maximum, compared to the epilimnion and hypolimnion layers of bulk water (Prokopkin, 2010). The change of the hydrochemical regime is also a phenomenon with an important impact (Mengis et al., 1997).

In the Lencauti and Cosauti sections the oxidation takes place more slowly, which shows considerable biochemical diminishes compared to the Naslavcea village. It can be assumed that this area is one of the more vulnerable in the case of the pollution treatment. In the upstream section of the Bac, downstream of the Bender city, the BOD_5 values are larger and growing compared to the sample from the Cosauti village, however the loads of organic matter are much higher. This fact leads to the equalization of the oxidation time of ammonia in these samples which are different as regards the composition of organic matter and the nitrogen mineral forms from water.

As one can see from Fig. 4, the anthropogenic accumulations lead to the increase of the exceeded MAC cases, that is a curve with peaks, which amplitude is growing to inferior sections, culminating in the Olaneshti one, and then returns to the normal shape up to the Palanca section.

A special case is the pollution of the Dubasari section. Upstream of this is the Rezina section (Fig. 4) where a minimum frequency of prevailing MAC was found for both ammonia and nitrites. Up to the Dubasari section, where many cases of the MAC overruns for nitrites have been found, there are not urban centers which would so strongly influence the aquatic environment. It appears that the impact on this segment is from the secondary pollution of lake sediments. The Lake Stanca-Costeshti is younger than Lake Dubasari, resulting in a lack of evident impact of the secondary pollution in the accumulation lake of the Prut River. This fact demonstrates the decrease of sustainability of the water treatment system on a segment of the the Nistru River.

The laboratory kinetic simulation from 2011 proves that in the sample taken from the Naslavcea section, the oxidation process occurred most quickly (8 days). In the previous publication (Spataru, 2011) there were presented data on solved oxygen in this section that was lower than in the downstream sections, while the value of BOD_5 is higher in comparison with the same sections.



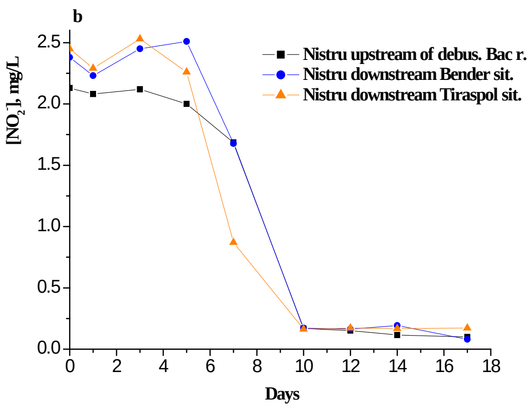


Fig. 5. The kinetics of the NH_4^+ ion oxidation in the samples from the Nistru River: (a) represents the sections upstream of the Bac River; (b) represents the sections downstream of the Tiraspol city

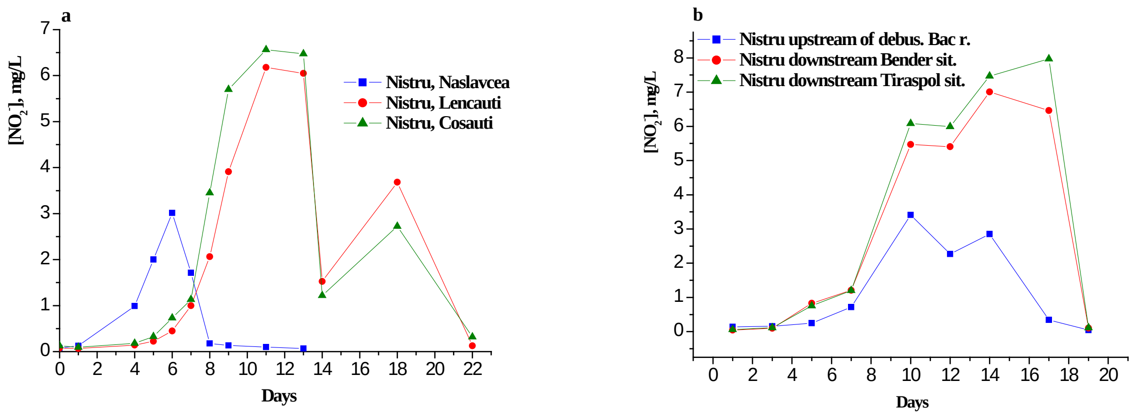


Fig. 6. The kinetics of oxidation of NO_2^- -ions in water samples taken from the Nistru River: (a) represents the sections upstream of the Bac River; (b) represents the sections downstream of the Tiraspol city

As one can see from Fig. 5a, 5b and 6a, 6b the oxidation of nitrites is more rapidly, although the ammonia oxidation is almost the same as in the samples from the Nistru River in the sections upstream of the Bac River, downstream of the Tiraspol city, compared with the Lencauti and Cosauti sections. This process keeps its high speed, even if in the lower sections of the Nistru River the organic load is greater. This fact confirms our earlier finding that the time of oxidation of all reduced nitrogen species depends proportionally on the organic matter amounts in natural waters (Spataru, 2011).

The diagram on Fig. 7, with all the accidental cases, demonstrates that the impact of the pollution is more evident in the winter and summer periods. The climate change mitigation the impact occurred in the spring, compared with the winter and summer. Due to the pollution of both wastewater and washing of land by the pluvial waters the River Prut becomes more affected. These situations can cause low dissolved oxygen concentrations due to the intensification of processes of oxidation and destruction, especially in the sections with an increased concentration of nitrites. The study of the samples of water from wells on the left side of the Prut River showed an obvious pollution with the nitrate ion (Table 3). Of 12 wells from which the water samples were collected within three years (2010-2012), in only two wells (in the Cuhnesti and Cobani villages) the water corresponds to the MAC level (for drinking water). Three of these contain nitrates over MAC, two contain nitrates over 2 MAC, and 5 of these contain over 3 and up to 13 MAC of nitrites. In dry seasons many wells remain without water, leaving the population of villages without any water supply sources.

4. Conclusions

Most of the main mineral parameters of the rivers Prut and Nistru waters, except ammonia and nitrates, correspond to the European statutory norms of "Drinking Water".

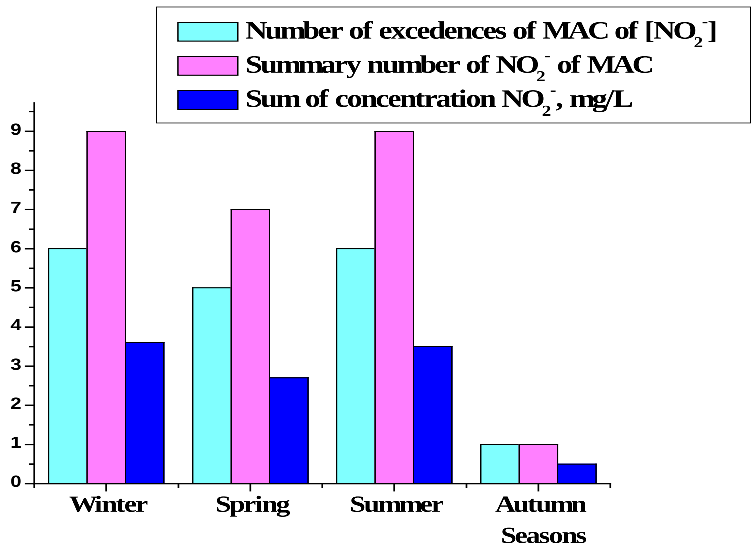


Fig. 7. The dynamics of the number of accidental cases (the exceeded MAC values) in the 2010-2012 yrs in the Prut and Nistru rivers (recorded by the State Hydrometeorological Service (MB, 2011))

Table 3. Nitrogen-containing species concentrations in groundwater

No	Sampling site/concentration	$[N\text{-}NH_4^+]$ mg/L MAC	$[N\text{-}NH_4^+]$ mg/L	$[N\text{-}NO_2^-]$ mg/L MAC	$[N\text{-}NO_2^-]$ mg/L	$[N\text{-}NO_3]$ mg/L MAC	$[N\text{-}NO_3^-]$ mg/L
1	Cobani village, dug well	0.39	0.08	0.02	0.09	9	0.7
2	Cobani well at the piquet frontier guard, dug well		0.00		0.00		**12.4**
3	Cuhneshti, dug well, grab sample		0.00		0.00		4.6
4	Bisericani, dug well, grab sample		0.00		0.00		**9.2**
5	Sirma, dug well, grab sample		0.00		0.00		**9.7**
6	Macareshti, well tube		0.00		0.00		**55.8**
7	Macareshti, dug well (1)		0.00		0.00		**62.2**
8	Macareshti, dug well (2)		0.00		0.00		**32.5**
9	Frasineshti, dug well		0.00		0.00		**19.8**
10	Aqueduct Branza		0.00		0.00		1.1
11	Colibashi, Dug well		0.00		0.00		**83.7**
12	Branza, dug well		0.00		0.00		**116.5**
13	Semeni, dug well		0.00		0.00		**19.6**

The dynamics of nitrogen mineral forms shows the impact of urban activities, where the stations for wastewater treatment do not work satisfactorily. It is necessary to improve the environmental management upstream of the border with the Ukraine for the Prut River and upstream of the Olaneshti section in the case of the Nistru River. Also the secondary pollution caused by sediments of the Lake dam Dubasari should be taken into account.

The water in the wells on the east side of the Prut River is polluted with nitrates and disappears in the most wells in dry periods. It is compulsory to run a series of projects, in order to fill the lack of drinking water in the abovementioned villages.

Acknowledgments

This work has been supported by the international program SCOPES 2009–2012 Swiss National Science Foundation Joint Research Project “Xenobiotic Input to the Prut River (XENOPRUT)”.

References

Blackall L.L., (2000), A Summary of Recent Microbial Discoveries in Biological Nutrient Removal from Wastewater, *Australasian Biotechnology*, **10**, 29-32.

Bradberry S.M., Gazzard B., Vale J.A., (1994), Methemoglobinemia caused by the accidental contamination of drinking water with sodium nitrite, *Clinical Toxicology*, **32**, 173-178.

Britto D.T., Siddiqi M.Y., Glass A.D.M., Kronzucker H.J., (2001), *Futile Transmembrane NH_4^+ Cycling: A Cellular Hypothesis to Explain Ammonium Toxicity in Plants*, Proc. of the National Academy of Sciences, USA, vol. 98, 4255-4258.

Britto D.T.; Konzucker H.J., (2002), NH_4^+ toxicity in higher plants: a critical review, *Journal* of *Plant Physiology*, **159**, 567-584.

Brunning-Fann C.S., Kaneene J.B., (1993), The effects of nitrate, nitrite, and N-nitroso compounds on human health, *Veterinary and Human Toxicology*, **35**, 521-538.

Cazac V., Ceres V., Gherghelegiu V., (2014), *Water Resources in the Territory of the Republic of Moldavia*, L.P. Estetini, Kishinev.

CD, (1998), Council Directive 98/83/EC on the quality of water intended for human consumption *Official Journal of the European Communities*, **L330**, 32-43.

Daum M., Zimmer W., Papen H., Kloos K., Nawrath K, Bothe H., (1998), Physiological and molecular biological characterization of ammonia oxidation of the heterotrophic nitrifier *Pseudomonas putida*, *Current Microbiology*, **37**, 281-288.

Gladchi V., Goreaceva N., Duca G., Bunduchi E., Borodaev R., Mardari I., Romanciuc L., (2008), Chemical composition and redox state of water from the medial Nistru River, *Environment (Mediul Ambiant)*, **39**, 20-28.

ISO 8466-1, (1990), Water quality - Calibration and evaluation of analytical methods and estimation of performance characteristics. Part 1: Statistical evaluation of the linear calibration function, On line at: https://www.iso.org/standard/15664.html.

Lewis M.A., (1992), The effects of mixtures and other environmental modifying factors on the toicities of surfactants to freshwater and marine life, *Water Reserarch*, **26**, 1013-1023.

Lin Y., Kong H., Wu D., Li C., Wang R., Tanaka S., (2010), Physiological and molecular biological characteristics of heterotrophic ammonia oxidation by *Bacillus* sp. LY. *World Journal of Microbiology and Biotechnology*, **26**, 1605-1612.

Linnik P., Zubenko I., (2000), Role of bottom sediments in the secondary pollution of aquatic environments by heavy-metal compounds, *Lakes & Reservoirs: Research & Management*, **5**, 11-21.

Martinelle K., Häggström L., (1993), Mechanisms of ammonia and ammonium ion toxicity in animal cells: Transport across cell membranes, *Journal of Biotechnology*, **30**, 339-350.

Matveeva N.P., Klimenko O.A., Trunov N.M., (1988), *Simulation of Self-Purification of Natural Treatment of Organic Pollutants in the Laboratory*, Gidrometeoizdat, Leningrad, Russia.

Mengis M., Gachter R., Wehrli B., (1997), Nitrogen elimination in two deep eutrophic lakes, *Limnology and Oceanography*, **42**, 1530-1543.

MB, (2011), Monthly Bulletin, Ambient Quality in Republic of Moldova, Chisinau, On line at: www. meteo.md.

Muller B., Berg M., Yao Z.P., Zhang X.F., Wang D., Pfluger A., (2008), How polluted is the Yangtze river? Water quality downstream from the Three Gorges Dam, *Science of the total environment*, **402**, 232-247.

Müller T., Walter B., Wirtz A., Burkovski A., (2006), Ammonium Toxicity in Bacteria, *Current Microbiology*, **52**, 400-406.

NRSERM, (2011), National Report on the State of the Environment in the Republic of Moldova 2007–2010, Chisinau, 44, On line at: www.mediu.gov.md.

Pernet-Coudrier B., Qi W., Liu H., Muller B., Berg M., (2012), Sources and pathways of nutrients in the semi-arid region of Beijing−Tianjin, China, *Environmental Science and Technology*, **46**, 5294-5301.

Philips S., Hendrikus J., Laanbroek, Verstraete W., (2002), Origin, causes and effects of increased nitrite concentrations in aquatic environments, *Reviews in Environmental Science and Bio-Technology*, **1**, 115-141.

Prokopkin G., Mooij W.M., Janse J.H., Degermendzhy A.G., (2010), A general one-dimensional vertical ecosystem model of Lake Shira: description, parameterization and analysis, *Aquatic Ecology*, **44**, 585-618.

Sandu M., Lozan R., Ropot V., (1989), Determination of nitrate and nitrite in natural waters, *Chemistry and Technology of Water*, **3**, 120-125.

SR EN 26777:2002/C91:2006, (2006), Water quality - determination of the content of nitrites. The method of the spectrometry of molecular absorption.

Spataru P., (2011), *Transformation of organic matter in the surface waters of the Republic of Moldova*, PhD thesis, Institute of Chemistry of the Academy of Sciences of Moldova, Chisinau, Republic of Moldova.

SR ISO 7890-3, (2000), Water quality - The determination of the content of nitrates. The part 3: The spectrometric method with sulfosalicylic acid, On line at: http://agris.fao.org/agris-search/search.do?recordID=XF8981389.

State Register (2007), State of natural mineral water, soft drinks and bottled drinking publshed: 24.08.2007, *Official Monitor* No.131-135 art. No 970 (in Romanian), Kishinev, Republic of Moldavia.

Teodoru C.R., Friedl G., Friedrich J., Roehl U., Sturm M., Wehrli B., (2007), Spatial distribution and recent changes in carbon, nitrogen and phosphorus accumulation in sediments of the Black Sea, *Marine Chemistry*, **105**, S52-S58.

Van Leeuwen, F.X.R., (2000), Safe drinking water: the toxicologist’s approach, *Food and Chemical Toxicology*, **38**, 51-58.

Weng Y.M., Hotchkiss J.H., Babish J.G., (1992), N-nitrosamine and mutagenicity formation in Chinese salted fish after digestion, *Food Additives and Contaminants*, **9**, 29-37.

Zubcov E., Bagrin N., Ungureanu L., Biletchi L., Borodin N., Bogonin Z., (2011), Dynamics of the hydrochemical parameters and the quality of the Prut River, *Bulletin of the Academy of Sciences of Moldavia. Life Sciences (Buletinul Academiei de Ştiinţe a Moldovei Ştiinţele vieţii)*, **313**, 103-110 .

Zubcov E., Ungureanu L., Ene A., Zubcov N., Bagrin N., Borodin N., Lebedenco L., Biletchi L., (2010), Assessment of chemical compositions of water and ecological situation in Dniester river, *Journal of Science and Arts*, **10**, 47-52.