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NITROGEN-BASED NUTRIENT POLLUTION OF WATER BODIES: IMPACT ON THE AQUATIC ECOSYSTEMS AND HUMAN HEALTH

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As water is an indispensable resource, ensuring multiple ecosystems services, its protection is of most high interest. To prevent and reduce the severe impact generated by anthropogenic activities, like intensive agriculture, more efforts are needed. In view of this, the paper aims to give an overview of water bodies pollution with nitrogen-based nutrients and the impact that this type of pollution has on aquatic ecosystems as well as human health. From this perspective, the dynamic of the status of water sources in Romania is presented for a period of 12 years (2011–2022) and correlation with the associated diseases (*e.g.* methemoglobinemia) are made.

Keywords: nitrogen-based nutrients, nitrate, water pollution, methemoglobinemia

Water is one of the essential primary resources necessary for human survival. With the rise of industrialization, agricultural production and urban life, freshwater consumption has also increased globally in the past 100 years, resulting in environmental degradation and resources depletion. The release of industrial and municipal wastewaters into the environment, inadequately treated or without any prior treatment, has a negative impact on water bodies that support life, ultimately affecting human health and sustainable social development. In countries where sanitation and treatment facilities are lacking, it is estimated that over 80% of the released effluents pose serious threats to the aquatic systems[1]. Water pollution is also closely linked to agricultural activities, which contaminate water especially with fertilizers (nitrogen and phosphorus nutrients) and pesticides but contributing also to the increase of the content of water bodies in dissolved salts, sediments, and pathogens. The two elements that most typically limit both terrestrial and aquatic primary productivity are nitrogen (N) and phosphorus (P). These key nutrients are frequently applied as fertilizers[2] and their transfer from land to water bodies can imbalance the aquatic ecosystems.

This work aims to present the sources of pollution of water bodies with nitrogen-based nutrients and the impact that this type of pollution has on aquatic ecosystems as well as human health. From this perspective, an overview of the status of water sources in Romania is presented for a period of 12 years, 2011–2022.

WATER POLLUTION WITH N-NUTRIENTS

Sources of the nitrogen-based nutrient contamination of water bodies can be both anthropogenic and natural. Main anthropogenic sources are large-scale agricultural activities, industrial wastewaters, fossil fuels combustion and mining practices. Nitrogen compounds are used and/or synthetized in many industrial processes, among them: preservatives in the food industry, detergents components (nitriloacetate), agents for superconductors and ceramics development, rocket fuel oxidizer (N_2O_4), explosive component breakdown, sewage water treatment plant byproducts, landfill leachate etc[3]. Natural sources like ant hills, termite mounds and biological soil crusts have been identified as substantial contributors to nitrate contamination of groundwater in dry and semi-arid areas with low or no agricultural activity[4].

Many terrestrial, freshwater and marine ecosystems depend to a great extent for species diversity, dynamics and overall health on the availability of N[5], which is a primary essential nutrient entering the composition of numerous biomolecules: proteins, DNA, chlorophyll etc.[6]. However, excessive input of nutrients can negatively impact the aquatic ecosystems. In the soil, N has several loss mechanisms, and many agricultural crops have low nitrogen usage efficiency[7]. That is why, in intensive agriculture, the application of commercial fertilizers is resorted to, both inorganic (mostly $NaNO_3$ and NH_4NO_3) and organic (urea and amines). After application of organic fertilizers to soils the mineralization process begins, inorganic nitrogen is released and absorbed directly by the plants or transformed to other forms through the oxidation process. The rate of mineralization depends on several factors: agricultural management, microorganisms, soil properties, temperature, water content, and the type of organic fertilizer applied. The inorganic forms are particularly soluble for easy assimilation by crops and are the main sources of nitrogen compounds of water[8].

From the soil, excess nitrogen is lost in ionic or gaseous form by leaching, or denitrification and volatilisation, respectively. The nitrate ions which are not absorbed by plant roots, are easily washed away from the soil, and enter surface or groundwater by surface runoff or percolation[9]. In the aquatic systems, microorganisms play a key role in nitrogen transformation via oxidation and reduction processes. Organic nitrogen compounds are degraded by ammonification, releasing ammonium (NH_4^+) that are further oxidized to nitrite (NO_2^-), and then to nitrate (NO_3^-) by nitrification and eventually converted into dinitrogen gas (N_2) through denitrification and anammox processes. The NO_3^- and NO_2^- produced by nitrification in streams and rivers could be easily transferred to groundwater. In anaerobic media, NO_3^-/NO_2^-, can serve as electron acceptor for chemoorganoheterotrophic bacteria which convert these oxidised forms of nitrogen into ammonium by the so called DNRA process, dissimilatory nitrate reduction to ammonium, which could act as a sink of bioavailable nitrogen (Fig. 1). These processes significantly impact the transport and transformation of nitrogen in the aquatic systems.

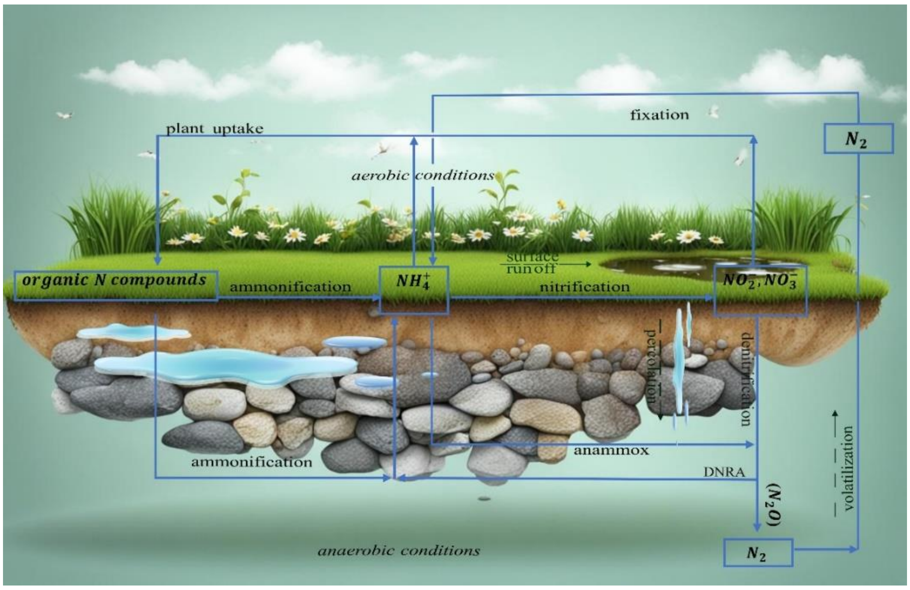


Figure 1. The cycle of nitrogen in aquatic systems: sources, transformation, and flux.

Fossil fuel combustion is the main source of global emissions of nitrogen oxides (NOx), especially nitric oxide (NO), to the atmosphere alongside emissions from soil denitrification (mostly nitrous oxide, N_2O and NO). Removal of NO_x from the atmosphere is achieved by dry and wet depositions. Thus, nitrogen oxides can enter the aquatic systems by dry deposition, directly or after chemical transformation into gaseous HNO_3, particulate NO_3^-, or HONO. While NO_3^- can also enter through wet deposition when it is incorporated into water particle in clouds or precipitations[10].

The removal, processing and disposal of vast volumes of rocks and wastes near water catchments in mining activities alter the status of freshwaters by contaminating them with toxic chemicals. According to Li *et al*. (2023), surface rocks account for approximately 20% of global nitrogen and release into aquatic systems up to 3×10^{10} kg of N each year[11]. Another important source of nitrogen compounds, NO_3^- and NH_4^+ is the residues of explosives (*e.g*. ammonium nitrate) used in mining[12].

IMPACT OF NUTRIENT POLLUTION ON AQUATIC ECOSYSTEMS AND HUMAN HEALTH

Excessive amounts of N-nutrients are increasingly reported to unbalance aquatic systems and to pose a risk to the human health. In the last decades, N-nutrients contamination has increased exponentially in both surface and underground waters with risks for aquatic and terrestrial ecosystems[13]. Along with freshwater systems, estuary and marine ecosystems have suffered degradation due to the accelerated transit of N-nutrients through the land-water interface to the coastal area due to urbanization, population growth and increased use of fertilizers[14].

Surface waters bodies with high NO_3^- concentration might suffer eutrophication, a process responsible for the rapid growth of primary producer, as N is a limiting nutrient for protein synthesis and chlorophyll production[15]. When human activities are the main ones responsible, the process is known as cultural eutrophication. The major effect of cultural eutrophication is the algae and cyanobacteria blooms, leading eventually to accumulation of toxins and depletion of the dissolved oxygen in the bodies of water[16]. Damages due to eutrophication are substantial and include changes in biological community composition with losses in biodiversity and ecosystem services, increased expenditure on water treatment and negative effects on economic activities and tourism[17].

Over the past two decades, nitrate has garnered a lot of research interest as a widespread groundwater contaminant[18–20]. In most European countries, nitrate contamination is responsible for the loss of 4% of fresh water sources such as aquifers[21]. Nitrate and nitrite contamination of drinking water sources is of main concern because drinking water is one of the primary ways of exposure to these contaminants for the human population.

With the ingestion of drinking water with a nitrate concentration of more than 50 mg/L, the digestive system converts an appreciable amount of NO_3^- into NO_2^- due to the action of the microbiota. A conversion which is more effective for babies under the age of 3 months. The resulting NO_2^- which enters the blood stream oxidizes the iron on the porphyrin active center of hemoglobin generating methemoglobin, which is unable to bind and transport oxygen[22]. High level of methemoglobin resulting in methemoglobinemia, pathology known also as "*Blue Baby Syndrome*" due to the more frequent cases of infant's cyanosis as results of their hypersensitivity to the exposure to NO_3^- / NO_2^-.

The presence of nitrate in the organism is also linked to an increased prevalence of some cancers of the stomach and esophagus as well as other cancers, according to epidemiological studies carried out[23]. The incriminated for the carcinogenic effect are the nitrosamines formed from the interaction of biomolecules and nitrites resulted from the reduction of nitrates under specific circumstances of gastric achlorhydria[24, 25].

SURFACE AND UNDERGROUND WATER RESOURCES IN ROMANIA

Legislative aspects and monitoring of drinking water sources

The Water Framework Directive 2000/60/EC (WFD)[26] sets standards for halting the deterioration of all water bodies in the European Union (EU) and achieving the "good ecological state" of Europe's rivers, lakes, and groundwater. The main objectives of this Directive are: (i) protection of all forms of water (surface, ground, inland, and transitional waters); (ii) recovery of ecosystems in and around these waters; (iii) reducing pollution in water bodies and (iv) ensuring sustainable water use by individuals and businesses.

Protecting human health involves ensuring the quality of water intended for human consumption as wholesome and clean water and improving access to drinking water. To ensure the safety of drinking water, each member state must establish water supply zones and monitor them in accordance with the minimum control requirements laid down by the WFD. The supply zones are classified based on the quantity of water consumed and the number of people served. Water supply zones that provide over 1,000 m^3 of water daily on average or serve more than 5,000 people are known as "large water supply zones" (LWSZ). While water supply zones that provide an average of less than 1,000 m^3 but superior of 10 m^3 of water per day or serve 50 to

5,000 people are classified as "small water supply zones" (SWSZ); and those that provide less than 10 m³ of water per day or serve fewer than 50 people are included in "very small water supply zones".

The water quality monitoring system in Romania is developed based on the WFD. From the point of view of drinking water supplies, WFD was initially transposed in the Law of Drinking Water Quality 458/2002, amended subsequently in 2004 by the Law no. 311 and Government Decision no. 974 and finally replaced by the Ordinance no.7 of January 18, 2023[27–30].

There are two main bodies responsible for water monitoring at the national level. The *National Administration of Romanian Waters* administers the infrastructure of the National Water Management System consisting of reservoirs, flood protection dykes, canals, inter-basin diversions, water intakes and other specific works, as well as the infrastructure of the national hydrological, hydrogeological and quality monitoring systems of the water resources in the public domain, with the aim to manage in a unified way the surface and underground water resources throughout the country. The second body, the *Public Health Directions of Counties and of the Municipality of Bucharest (PHDs)*, is subordinate to the Ministry of Health and is responsible for monitoring the quality of drinking water in the centralized distribution system as well as from individual sources. The integration of the data from all PHDs is done by the *National Institute of Public Health* (*NIPH*)[31], which coordinates public health activities at the national level.

To assess and ensure the quality of water intended for human consumption a particular importance is given to the monitoring of the water in the centralized system which ensure the largest quantity of potable water in Romania, around 60 % of the national requirement. In this purpose, each Water Treatment Plant (WTP) foresees two types of monitoring: operational monitoring (OM) conducted by the water supplier and audit monitoring (AM) conducted by the county's public health department. However, the importance of the monitoring of other drinking water sources such as public or private wells can not be neglected, PHDs being directly involved in this activity.

The dynamic of drinking water quality from the perspective of N-nutrients pollution

As a response to the applicable legislation, the DPHs carry out annually the AM of drinking water quality for LWSZ and SWSZ of the centralized system and integrate the data received from the OM carried out by drinking water operators. In addition, through the national health programs, DPHs also monitor the quality of the water supplied from public wells and springs and take action to inform the public about water quality. The obtained data are processed and reported to the NIPH according to the internal methodologies. The data are public and part of them are presented by NIPH as annual reports[32].

Based on these public data, the present work presents a picture of the N-nutrients (NO_3^-, NO_2^- and NH_4^+) dynamic in drinking water in Romania for a period of 12 years, 2011–2022. Unfortunately, not all published reports contain a complete set of data, or the data are presented in different manners along the time. This is why there are some gaps for the investigated period.

The chemical analysis of the three parameters, NO_3^-, NO_2^- and NH_4^+, which have a maximal admissible concentrations (MAC) in the drinking water of 50 mg/L, 0.50 mg/L and 0.50 mg/L, respectively, were performed in the county DPHs laboratories, taking into account international standards, national legislation, and internal procedures specific to each individual laboratory (*e.g.* SR EN ISO 7150-1:2001, SR EN ISO 7150-1:2001 and SR EN ISO 7890-3:2000).

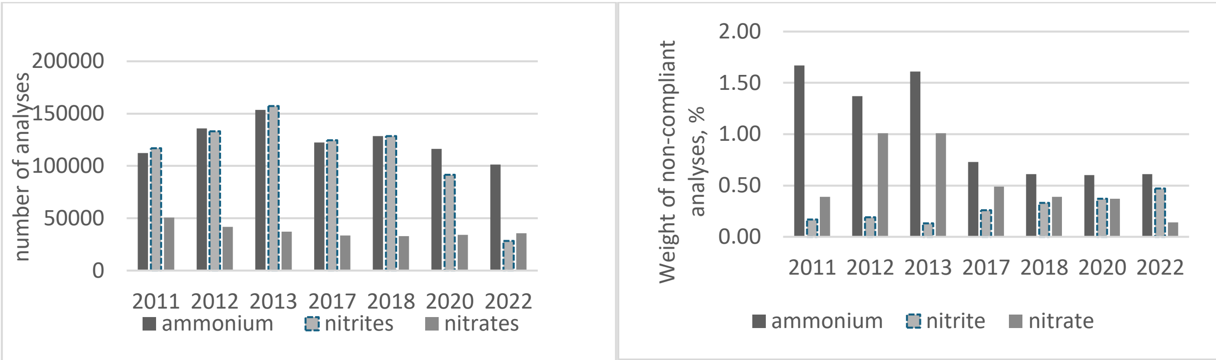
Centralized water supply system

Starting from a minimum of 33,500 to over 150,000 analyses were performed annually for each parameter (Fig 2a), the number of analyses depending on number of LWSZ and SWSZ but also on the non-compliant results. The constant trend of growth of the population's access to drinking water supplied in the centralized system, in both rural and urban areas, has led to an increase of LWSZ number, from 298 in 2011 to 361 in 2022. For the first three years (2011–2013) the proportion of non-compliant analyses exceeded 1.5% for ammonium and was close to 1.0% for nitrate (Fig. 2b), which was reflected in the higher number of samples analyzed for these parameters.

Nevertheless, the second part of the investigated period (2017–2022) is characterized by an increase in drinking water quality. The trend could be due to the modernization of water treatment systems, the realization of new capture fronts and the removal of drills where the quality parameters have recorded frequent exceeds of the MAC. Thus, the percentage of non-compliant analyses for ammonium and nitrate ions have decreased, from 1.67% in 2011 to 0.61% in 2022 and from 1.01% in 2012 to only

0.14% in 2022, respectively. Regarding the nitrite ions concentration, a small but constant increasing tendency was observed; the percentage of non-compliant analyses for this parameter increases from 0.17% in 2011 to 0.47% in 2022 (Fig. 2b).

In this context, a potential case could be the hyperchlorination (excessive chlorination during the water treatment) when NO_2^- can be formed as by-product in the NH_4^+, ammonium oxidation oxidation[33].



(a) **(b)**

Figure 2. Monitoring of NH_4^+, NO_2^- and NO_3^- parameters for drinking water sources in Romania: (a) total number of analyses performed *per* year; (b) percentage of non-compliant analyses.

Public wells and springs

In Romania, 31% to 42% of drinking water sources are groundwater bodies (Fig. 3) exploited in centralized and non-centralized systems or individually[34–42]. This emphasizes the importance of the monitoring programs of the DPHs for these sources, especially in the case of individual water supply where groundwater bodies are almost exclusively used.

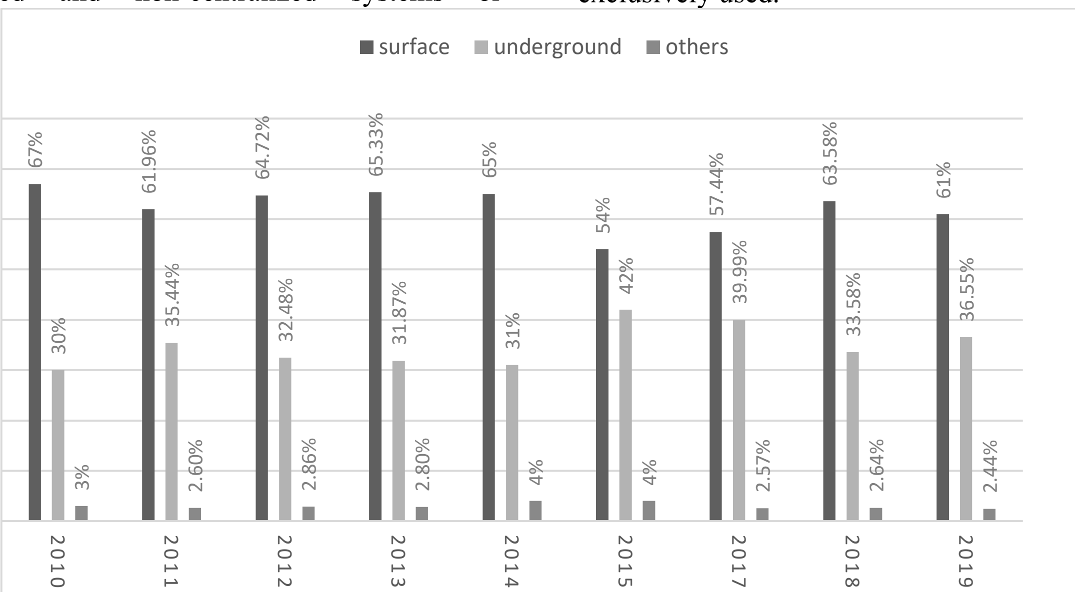
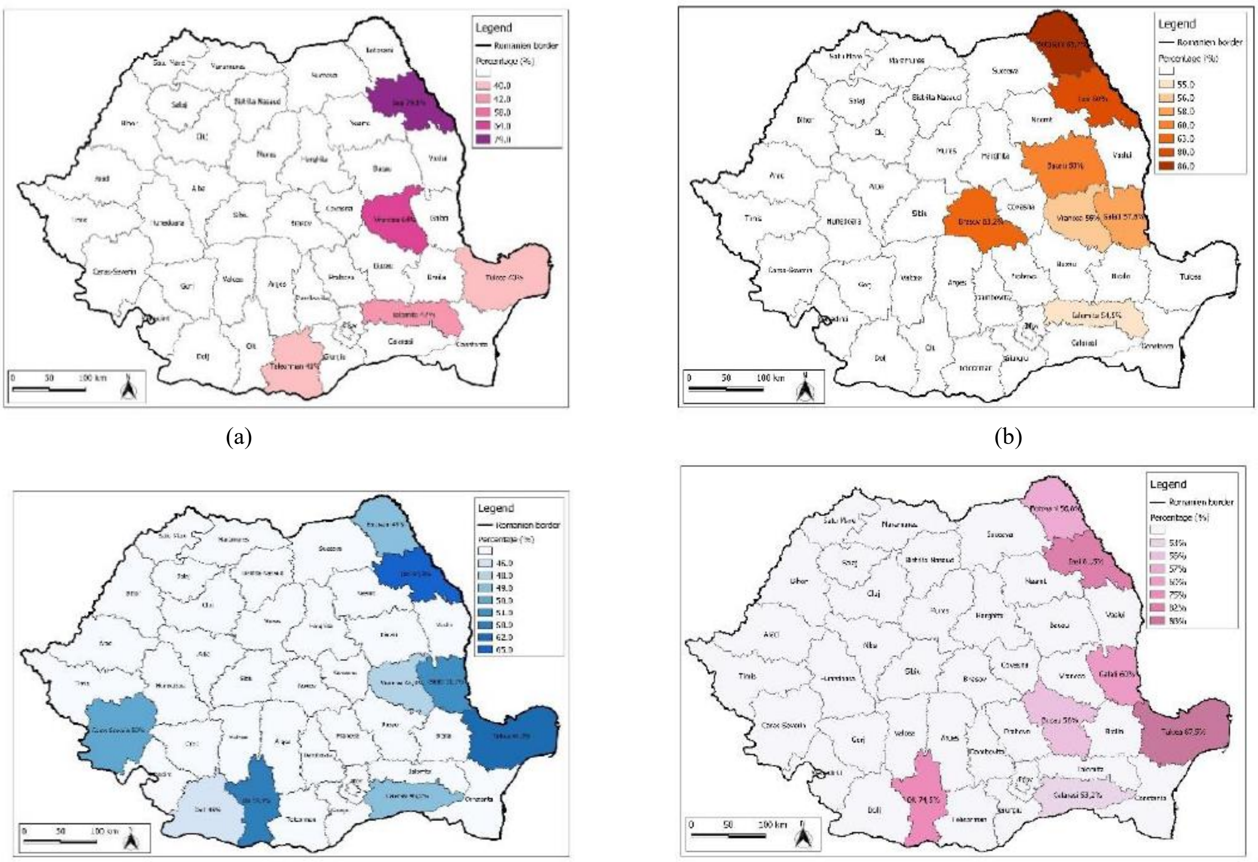


Figure 3. Type of sources for drinking water supply in Romania (others: artificial recharged aquifer, water filtering through sandbank/gravel).

The DPHs program aims to identify and assess the qualities of individual sources, public wells and artesian waters, used for human consumption. In most of the counties there are non-conformities of these water sources, which lead to actions to be taken in order to warn the population of the risk of consuming water from contaminated sources. Thus, contaminated sources were labelled with "*water not suitable for drinking*" or "*water not suitable for drinking for infants and young children*" and kept in the monitoring program until the problem is solved. Additionally, potable water was provided for infants and children up to 3 years[43].

A short overview of the status of the groundwater sources from point of view of N-nutrients contamination in the period 2018–2021, for which complete sets of data were available, is presented in the following[44]. For this period, Iasi is by far the most affected county with around 80% of the ground water sources exciding the MAC for NO_3^-, excepting the year 2020 where the percentage was of 64.5. The twelve most affected counties (Botoșani, Brașov, Călărași, Caraș-Severin, Dolj, Galați, Iași, Ialomița, Olt, Teleorman, Tulcea and Vrancea) with more than 40% of non-compliant samples for NO_3^- are found, excepting Brașov, in the East and South regions where intensive agricultural practices are common (Fig. 4). It should be noted that for NH_4^+ and NO_2^- the MAC are less frequently exceeded. A serious situation has been recorded for NH_4^+ in Sălaj county with 41,7%, 77,8% and 42,9% of exceeded CMA in 2019, 2020 and 2021, respectively. While only around 11% of groundwater sources has overcome the CMA for NO_2^-, in the case of Sălaj in 2019 and Olt in 2022.



(a) (b) (c) (d)

Figure 4. The Romanian counties with large number nitrate non-compliant groundwater sources from public fountains (over 40% of the monitored one) by year: (a) 2018; (b) 2019; (c) 2020 and (d) 2021.

As discussed in Section 2, the presence of nitrates in drinking water poses a risk to human health, especially to infants, through the development of methemoglobinemia. For the same period, 2018–2022 a total number of 113 cases of methemoglobinemia were reported in 36 Romanian counties (Fig. 5). With 21 cases, Iasi is in the top followed by Bacău with 13 cases and Vaslui with 10 cases. This founding directly corelates the number of methemoglobinemia cases with the percentage of the nitrate non-compliant groundwater sources from public fountains, although a more important contribution in the methemoglobinemia pathology is brought by individual sources, as could be observed from Figure 6.

According to the World Health Organization (WHO), in clinical epidemiological trials of methemoglobinemia associated with nitrates in drinking water, 97% of cases occur at concentrations above 44,3 mg/L, affecting, almost exclusively, persons under the age of 3 months[49]. In Romania, methemoglobinemia has most frequently been associated with private wells (Fig. 6), the most affected age group being 1–3 months, ranging between 55.1% and 40% of the total cases from 2018 to 2021.

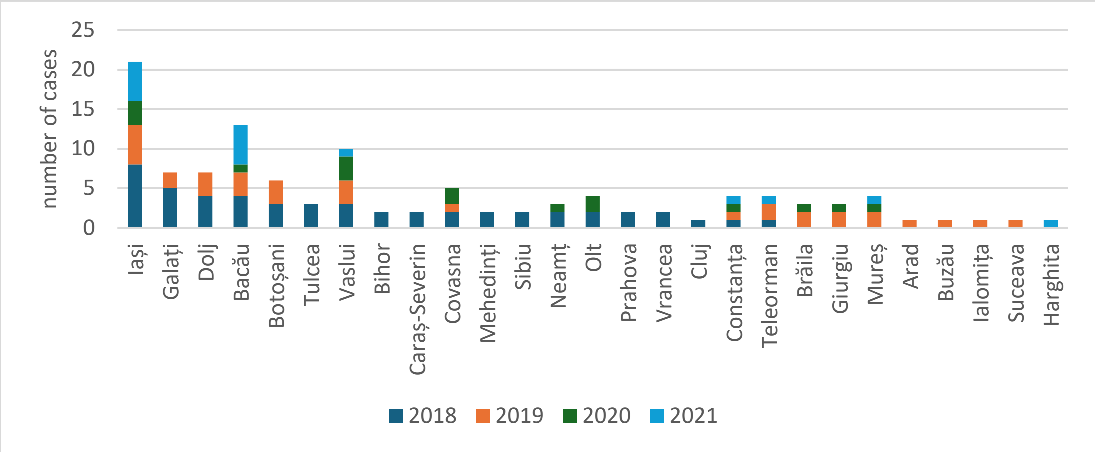


Figure 5. Cases of methemoglobinemia by counties between the years 2018–2021.

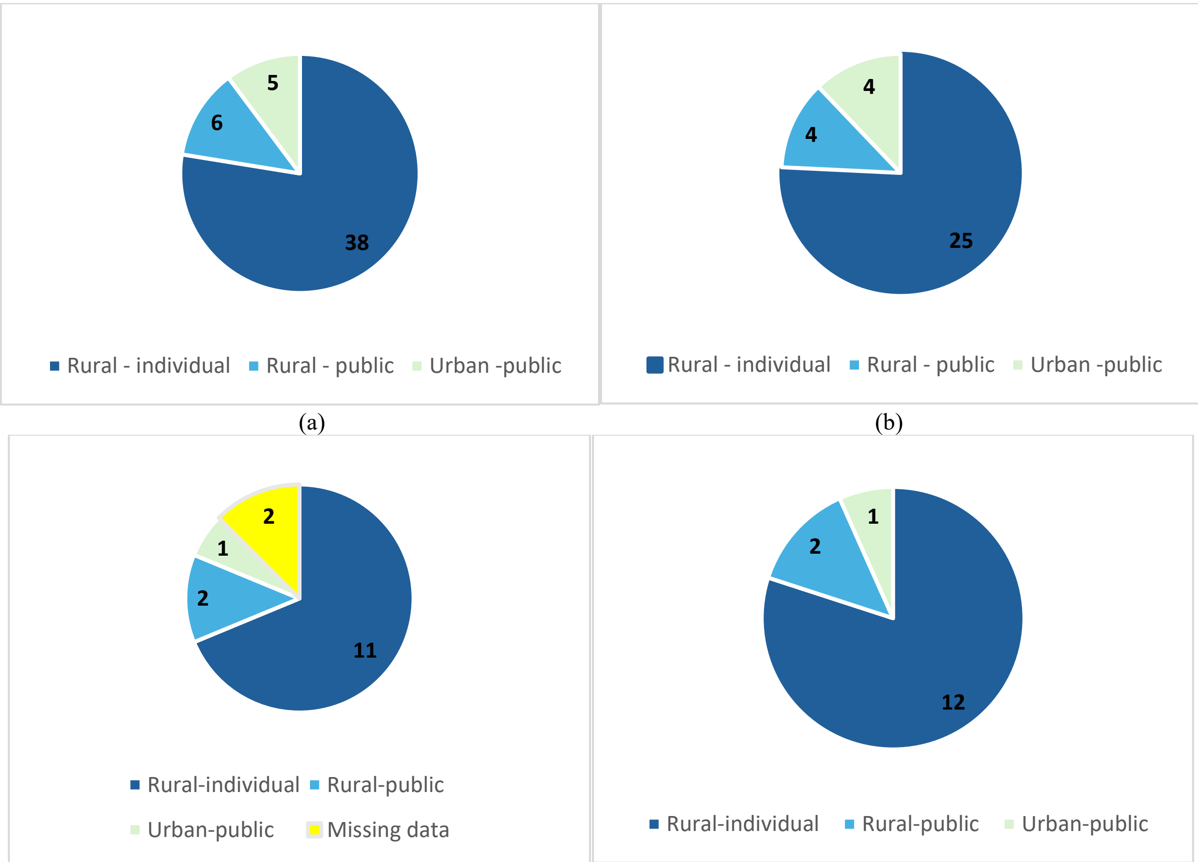


Figure 6. Distribution of methemoglobinemia cases as function of rural/urban areas and of individual/public source fountain type, by year: (a) 2018; (b) 2019; (c) 2020 and (d) 2021[45–48].

CONCLUSIONS

This paper reviews the nitrogen-based nutrient pollution of water bodies and its impacts and focus on the quality of surface and underground water sources in Romania. The literature data accounts for a worldwide increasingly contamination of waters with N-nutrients in the past two decades with severe effects on the aquatic ecosystems and human health.

Romania is part of the general picture with a non-negligible contamination of the surface and underground water resources with N-nutrients, especially with NO_3^-. However, for the period investigated (2011–2022) an increasing trend of the drinking water quality was observed from point of view of nitrate and ammonium parameters, most likely due to the modernization of centralized water treatment systems. In contrast with the centralized system, the non-centralized system of public and individual (private) fountains still records frequent exceedances of the CMAs. However, it should be mentioned that, following the implementation of national health programs for monitoring public fountains, there is a tendency to decrease the number of cases of methemoglobinemia by almost 70% in the last four years. This program unfortunately does not cover the individual fountain and a high risk persists for these drinking water sources which are responsible for the most methemoglobinemia cases reported.

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