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GROUNDWATER QUALITY IN THE REPUBLIC OF MOLDOVA AND TECHNOLOGIES FOR ITS POTABILIZATION

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Abstract. This paper summarizes data on the chemical composition of groundwater from artesian and phreatic wells across various regions of the Republic of Moldova. A comparative analysis of water samples was conducted to identify the parameters that most frequently exceed maximum permissible concentrations in both types of sources. Furthermore, the paper presents research findings on groundwater treatment technologies specifically targeting the removal of ammonia and ammonium ions.

Keywords: underground water, chemical composition, potabilization technology.

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Introduction

Water is the essence of life; without it, life on Earth would not exist. Both the animal and plant kingdoms require water to maintain the physiological, chemical, and microbiological processes essential to living organisms. For humans, access to fresh water is of paramount importance. However, due to global population growth, improved living standards, and intensive industrial and agricultural development, freshwater scarcity is becoming increasingly alarming. This global water crisis involves not only fresh water quantity but also its quality. Human activities generate vast amounts of wastewater that are often discharged untreated, effectively removing significant volumes of fresh water from the natural cycle. This further aggravates the challenges of providing the population with high-quality water supplies.

The consumption of high-quality water in sufficient quantities is essential for human health. Access to clean water is crucial for reducing the burden of disease and improving quality of life [1]. Due to inadequate water sources, poor sanitation and hygiene, 3.4 million people die each year from water-related diseases [2]. Freshwater on Earth is sourced from both surface and underground reservoirs. Due to population growth and anthropogenic activities, the reliance on groundwater has increased significantly in recent years. Indeed, groundwater serves as the sole source of drinking water for at least two billion people worldwide [3]. The physical, chemical, and biological characteristics of water serve as quality indicators for groundwater sources [4]. Issues regarding the quality of groundwater used for drinking and irrigation, as well as sources of pollution and chemical parameters exceeding maximum allowable limits in various geographical areas, are extensively documented in scientific literature [5-16]. Analysis of these sources highlights frequent contamination of groundwater with heavy metal ions, nitrates, nitrites, fluoride, hydrogen sulphide, and other pollutants.

In the Republic of Moldova, groundwater accounts for 65% of the total water volume consumed by the population. Monitoring results of water quality in centralised underground drinking water supply systems reveal significant non-conformity in both chemical and microbiological parameters. The most critical situation is observed in rural areas, where phreatic wells serve as the primary water source. Research conducted by various accredited laboratories in Moldova indicates that approximately 61% of water from artesian wells and 84% from phreatic wells do not meet sanitary standards for chemical composition. The specific indicators exceeding maximum allowable concentrations (MAC) differ between these two sources. Artesian wells are typically characterized by elevated levels of hydrogen sulphide and soluble sulphides, ammonia and ammonium ions, sodium ions, fluoride ions, total iron, and manganese, with water hardness below 5°dH. In contrast, phreatic wells frequently exhibit excessive levels of nitrates, nitrites, sulphates, chlorides, and total dissolved solids (TDS), along with high hardness values [17].

The quality of drinking water from underground sources also fails to meet bacteriological standards. These sources are primarily impacted by livestock farms, landfills, fertilizer and waste storage facilities, and the absence of adequate wastewater treatment systems [18,19].

The chemical composition of groundwater is influenced by both geological and anthropogenic factors. Notably, anthropogenic factors exert a significantly greater impact on the chemical composition of water from phreatic wells compared to that from artesian wells [20].

To ensure the supply of high-quality drinking water in compliance with Law no. 182 (December 19, 2019) [21], it is essential to develop high-performance technologies for removing chemical constituents from groundwater that exceed Maximum Allowable Concentrations (MAC) and to be respected the Government Decision no. 931 of 20.11.2013 [22].

Previous research investigated the removal of tetrachloroethene (PCE) from groundwater using granular activated carbons produced *via* thermal and chemical activation [23]. Similarly, the effectiveness of a composite material-activated carbon impregnated with zero-valent iron-for treating water contaminated with chlorinated organic substances was explored in [24]. Methods for removing iron and manganese ions using various disinfectants are detailed in the monograph by Musa, S. *et al.* [25], while the authors Kabuba, J. *et al*. [26] provide a comprehensive overview of physical, chemical, and thermal treatment techniques designed to enhance ground water quality. Further studies by Ayoub, M. addressed the improvement of parameters such as pH, turbidity, dissolved oxygen, sulphates, chlorides, and manganese through aeration and sedimentation processes [27]. Additionally, Kabuba, J. *et al*. identified optimal conditions for the adsorption of ammoniacal nitrogen onto activated carbon derived from waste tires [26]. The use of a compact unit for nitrification and denitrification processes followed by filtration through activated carbon to remove total nitrogen from groundwater contaminated with ammonium and ammonia ions are studied in [27]. A review of the literature indicates that while groundwater treatment technologies are well-established globally, they lack universal applicability. Research emphasizes the necessity of developing tailored technological solutions for each specific source, accounting for its unique chemical composition.

This paper presents the results of a chemical quality assessment of groundwater across various geographical regions of the Republic of Moldova. Furthermore, it details research findings regarding the development of a remediation technology for ammonia and ammonium ions. Specifically, the study focuses on groundwater from the Onitcani locality in the Criuleni district, where concentrations of these pollutants exceed current sanitary limits.

Experimental

Materials and methods

Sample collection and analysis

During the 2024–2025 period, a total of 209 water samples were collected from the districts of Criuleni, Ialoveni, Singerei, Hincesti, Straseni, Anenii Noi, Falesti, Briceni, Telenesti, Stefan Voda, Causeni. Cimislia of the Republic of Moldova. Particular attention was paid to sampling, storage and analysis procedures to avoid contamination. The samples were taken in 1.5 litre plastic containers. The water samples were placed in a refrigerator and transported within a maximum of 5 hours to the laboratory for analysis. The analysis of priority pollutants was performed in a laboratory accredited according to ISO 17025:2018 for water quality.

All water samples were analysed for a comprehensive range of chemical parameters, including hydrogen sulphide and dissolved sulphides, ammonia and ammonium ions, nitrites, nitrates, total hardness, sodium, iron, fluorides, sulphates, chlorides, oxidability, and total dissolved solids (TDS), as well as toxic metals (total Cr, Ni, Cd, Pb, Cu, Zn). All parameters were determined according to standard analytical techniques.

Specifically, total hardness was determined by EDTA titrimetry [28]; sodium ions by flame emission spectrometry [29]; and total dissolved solids by the gravimetric (weight) method [30]. Spectrometric methods were employed for several parameters: iron ions [31], fluorides (using alizarin complexone) [32], ammonia and ammonium ions (Nessler's reagent) [33], and nitrates [34]. sulphates were measured turbidimetrically [35], while chlorides were analysed *via* Mohr's volumetric titration [36]. Hydrogen sulphide and dissolved sulphides were determined by iodometry [37], and the permanganate index was assessed by titrimetry [38]. Toxic metal concentrations were analysed using atomic absorption spectrophotometry (AAS) [39]. The results are summarized in Tables 1 and 2.

Development of groundwater treatment technology for ammonia and ammonium removal

To achieve this objective, water samples were collected from artesian well No. 2 in Onitcani (Criuleni district). Previously performed chemical analysis revealed total ammonia and ammonium concentration of 2.7 mg/L, which exceeds the maximum permissible limit (MPL) for drinking water by a factor of 5.4.

Sodium hypochlorite (NaOCl) in a 6% solution was employed as the oxidizing agent. The experimental procedure was conducted using 1 L of raw water in a 2 L glass reactor with oxidant dosages of 1.0 mL. Homogenization of the solution was achieved *via* aeration for 30 minutes.

Following the oxidation process, the residual concentration of ammonia and ammonium ions was measured. The treated solutions were then filtered through a column packed with local activated carbon obtained from walnut shells. The obtained results are presented in Table 3.

Results and discussion

The assessment of water suitability for drinking purposes was conducted according to the criteria set by national regulations - Law 182/2019. An objective criterion for the quantitative evaluation of water quality is the ratio of the measured concentration (C) of a parameter to its maximum allowable concentration (MAC), expressed as the C/MAC ratio. C/MAC values for all parameters that exceeded the MAC limits were calculated. Table 1 presents the MAC values as specified in Law 182/2019, the minimum and maximum exceedance values recorded, and the degree of exceedance for the analysed artesian wells.

Table 1

Chemical constituents of groundwater exceeding Maximum Allowable Concentrations (MAC).

Parameter	*Maximum allowable concentrations (MAC)*	*Minimum concentration found exceeding the MAC*	*Maximum concentration found exceeding the MAC*	*MAC exceedance ratio C/ MAC*	
				min	*max*
Hydrogen sulphide and dissolved sulphides, mg/L	0.1	0.15	33.0	1.5	330
Ammonia and ammonium ions, mg/L	0.5	0.58	7.51	1.16	15.0
Nitrites, mg/L	0.5	0.73	2.10	1.46	4.20
Nitrates, mg/L	50.0	63.9	249.9	1.28	5.00
Total hardness, min, °dH	5˚G	<0.28	4.20	17.8	1.19
Total hardness, max, mmol/L	7.0	7.5	21.0	1.07	3.00
Sodium ions, mg/L	200	217.5	1095.0	1.09	5.48
Iron ions (total), mg/L	0.2	0.33	5.90	1.65	29.5
Fluorides, mg/L	1.5	1.81	10.40	1.21	6.93
Sulphates, mg/L	250	290.7	954.4	1.16	3.82
Chlorides, mg/L	250	255.3	421.0	1.02	1.68
Permanganate index, mg O_2/L	5	6.06	26.0	1.21	5.20
Total dissolved solids (TDS), mg/L	1500	1583	2746	1.06	1.83

Table 2

Chemical constituents of groundwater exceeding Maximum Allowable Concentrations (MAC) in phreatic wells.

Parameter	*Maximum allowable concentrations (MAC)*	*Minimum concentration found exceeding the MAC*	*Maximum concentration found exceeding the MAC*	*MAC exceedance ratio C/ MAC*	
				min	*max*
Hydrogen sulphide and dissolved sulphides, mg/L	0.1	0.85	2.33	8.5	23.3
Ammonia and ammonium ions, mg/L	0.5	2.3	4.89	4.6	9.8
Nitrates, mg/L	50.0	65.5	677.6	1.3	13.6
Total hardness, max, mmol/L	7	10.1	31.1	1.4	4.2
Sodium ions, mg/L	200	221.0	490.0	1.1	2.5
Iron ions, mg/L	0.2	0.35	0.96	1.8	4.8
Fluorides, mg/L	1.5	1.79	-	1.2	-
Sulphates, mg/L	250	290.7	954.4	1.2	3.8
Chlorides, mg/L	250	283.7	3546	1.1	14.2
Total dissolved solids, mg/L	1500	1583.2	3012.0	1.1	2.0

Table 2 presents the MAC values established by Law No. 182 (December 19, 2019), along with the minimum and maximum concentrations exceeding these limits and the calculated MAC exceedance ratios for phreatic wells.

Research findings indicate that in most artesian well samples, Maximum Allowable Concentrations (MAC) were frequently exceeded for ammonia and ammonium ions (0.58–7.51 mg/L) in 70.7% of cases, followed by hydrogen sulphide and dissolved sulphides, (0.15–33 mg/L) in 43.1%, and sodium ions (218–1095 mg/L) in 37.9%.

Water hardness was evaluated based on two criteria: a minimum threshold of 5°dH and a maximum limit of 7 mmol/L. Since current national regulations do not specify a maximum allowable value for hardness, the limit of 7 mmol/L (in effect in Moldova until 2007) was adopted for this study. Results showed that 22.4% of samples fell below 5°dH (<0.28–4.2 °dH), while 35.3% exceeded 7 mmol/L (7.5–21 mmol/L).

Additionally, MAC exceedances were recorded for iron ions (0.33–5.9 mg/L) in 32.8% of wells, fluorides (1.81–10.4 mg/L) in 20.7%, permanganate index (6.06–26.0 mg O_2/L) in 11.2%, nitrates (64.0–149.9 mg/L) in 8.6%, and sulphates (290.7–954.0 mg/L) in 6.9%. Exceedances for total dissolved solids (1583–2747 mg/L), chlorides (255.0–421.0 mg/L), and nitrites (0.73–2.1 mg/L) were less frequent, occurring in 5.2%, 4.3%, and 1.7% of samples, respectively. The degree of exceedance varied significantly across all analysed parameters.

In water samples collected from phreatic wells, the most frequent MAC exceedances were observed for total hardness (10.0–31.0 mmol/L) in 67% of cases and nitrates (66.0–678.0 mg/L) in 50%. Total dissolved solids (1583.0–3012.0 mg/L) exceeded the limits in 20% of samples, followed by sodium ions (221.0–490.0 mg/L) in 18.1% of samples.

Other exceedances included sulphates (291.0–954.0 mg/L), ammonia and ammonium ions (2.30–4.89 mg/L), iron ions (0.35–0.96 mg/L), and hydrogen sulphide and dissolved sulphides, (0.85–2.33 mg/L) in 14.9%, 7.44%, 5.3%, and 4.3% of the analysed samples, respectively.

Fluoride content (1.79 mg/L) exceeded the MAC in only 1.06% of samples. Notably, permanganate index and nitrites did not exceed the MAC in any analysed samples, and water hardness never fell below the 5°dH threshold.

Tables 1 and 2 demonstrate that MAC exceedance ratios vary significantly across parameters, ranging from negligible to substantial. Additionally, while the presence of toxic heavy metals—including total chromium, nickel, lead, cadmium, copper, and zinc was analysed in samples from both artesian and phreatic wells, their concentrations remained within allowable limits in all cases.

Analysis of the results presented in Tables 1 and 2 indicates that out of 115 water samples from artesian wells, 111 (96.5%) failed to meet drinking water standards by at least one parameter. Similarly, out of 94 samples from phreatic wells, 93 (98.9%) did not comply with the established requirements.

Table 3

Quality indices of raw water and treated water after sodium hypochlorite treatment and activated carbon filtration (Artesian Well No. 2, Onitcani, Criuleni District).

No	*Parameter name and unit of measurement*	*Concentrations of chemical parameters in raw water, water after sodium hypochlorite treatment and after activated carbon filtration*		*Maximum Allowable Concentrations (MAC), mg/L*
		Probe No.2, raw water	*V_{NaClO}= 1.0 mL*	
1	Total hardness max, mmol/L	6.8	6.8	7.0
2	Nitrite (NO_2^-), mg/L	0.018	0.018	0.5
3	Ammonia and ammonium ions (total) (NH_3 + NH_4^+), mg/L	**2.70**	<0.05	0.5
4	Nitrates (NO_3^-), mg/L	2.78	2.78	50.0
5	Total iron (Fe), mg/L	<0.1	<0.1	0.2
6	Sodium (Na^+), mg/L	90.9	137.15	200
7	Sulphates (SO_4^{2-}), mg/L	147.6	147.6	250
8	Chlorides (Cl^-), mg/L	33.7	33.7	250
9	Fluorides (F^-), mg/L	0.57	0.57	1.5
10	Total dissolved solids, (105ºC), mg/L	599.6	599.6	1500
11	Hydrogen index (pH), pH unit	7.75	8.13	≥6.5-≤9.5

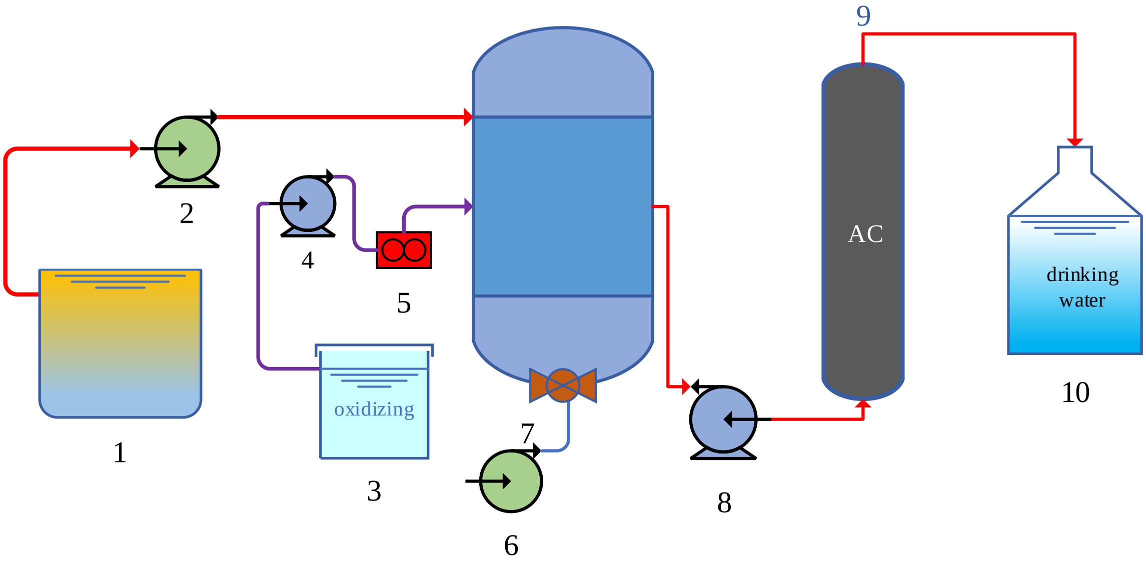

Figure 1. Technological scheme of the water treatment system for artesian well No. 2 (Onitcani, Criuleni District).
1 - raw water tank, 2 - feed pump, 3 - sodium hypochlorite solution tank, 4 - oxidant dosing pump, 5 - dosing unit, 6 - air compressor for aeration, 7 – reactor, 8 - pump feeding the filtration column, 9 - activated carbon (AC) filtration column, 10 - treated drinking water tank.

Analysis of the results in Table 3 demonstrates that using a 6% sodium hypochlorite solution as an oxidant (at a dosage of 1 mL/L) ensures the complete oxidation of ammonia and ammonium ions. Subsequent filtration through a column containing local activated carbon derived from walnut shells produces high-quality drinking water. The design of the water treatment system developed based on this study is illustrated in Figure 1.

Conclusions

Research findings indicate that over 95% of the analysed water samples from both artesian and phreatic wells do not meet the quality standards for drinking water.

Significant differences in chemical composition were observed between artesian and phreatic well water samples. Parameters exceeding the Maximum Allowable Concentrations (MAC) were specific to each source type. In artesian wells, exceedances were primarily recorded for ammonia and ammonium ions, hydrogen sulphide and dissolved sulphides, sodium ions, iron, and fluorides, while water hardness often fell below the minimum required limit. Conversely, phreatic wells were characterized by elevated levels of nitrates, hardness salts, sodium, sulphates, and total dissolved solids (TDS).

Notably, none of the analysed samples contained elevated concentrations of toxic heavy metals (total chromium, nickel, lead, cadmium, copper, or zinc).

The study highlights the poor quality of drinking water from both source types and emphasizes the urgent need for advanced purification technologies to address these contamination issues.

Effective treatment processes and technological schemes based on sodium hypochlorite treatment followed by activated carbon filtration were developed for the removal of ammonia and ammonium ions from groundwater sources. This process allowed for decreasing ammonia and ammonium ions from 2.7 to <0.5 mg/L.

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