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ASSESSING THE CHEMICAL COMPOSITION OF NATURAL WATER USING ANALYTICAL CHEMISTRY TECHNIQUES. A CASE STUDY IN THE ORHEI DISTRICT, REPUBLIC OF MOLDOVA

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Abstract. This study is primarily focused on evaluating the chemical composition of natural water in the locality of Cișmea, situated in the Orhei district, at the coordinates 47°24'56.0"N 28°45'05.9"E. The study includes an ad-hoc analysis of two types of water: surface water and underground water. General parameters were evaluated, such as pH, conductivity, hardness, chloride and sulphate content, as well as the content of certain chemical elements. The study results highlights significant deviations from the maximum admissible concentrations (MAC) for a series of indicators, such as As, Pb, Cd, Na, and B. The determined concentrations of these elements exceed the limits allowed by the legislation of Republic of Moldova and European Union: for As by 1.7−1.9 times; Cd by 3.4–3.5 times; Pb by 1.2–2.3 times; Na by 1.2–4.0 times and B by 1.6–3.3 times. Deviations of conductivity and sulphate parameters indicate the presence of a high level of dissolved solids in the groundwater of the locality's wells and springs. The study also signalled the presence of significant concentrations of some heavy elements, such as Ba, Tl and Bi, which are not regulated by current legislation.

Keywords: chemical composition of water, physico-chemical investigation, ICP-OES, heavy metal.

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Introduction

Water plays a pivotal role in our well-being, largely due to its chemical composition. It may contain substances that are essential for our health, but these require regular monitoring to ensure that the quality of drinking water remains optimal. The quality of water is largely influenced by the characteristics of the aquifer horizons, including factors such as water balance, dimensions, thickness, shape, storage capacity, discharge, hydraulic conductivity, transmissivity, coefficients of hydraulic diffusivity, efficient storage, recharge of aquifers, drainage possibilities, granulation or fracturing, permeability of aquifer rocks, their ability to retain and release water, and piezometric pressure, among others [1-4].

In the Republic of Moldova, water quality is primarily determined by the chemical composition of the rocks of the Moldovan Artesian Basin (MAB), which forms part of the Black Sea Artesian Basin and covers practically the entire territory of the Republic of Moldova. The MAB comprises horizons and aquifer complexes, weakly aquiferous and impermeable, differentiated by type and coefficient of permeability. The aquifer rocks, varying non-uniformly in thickness from 20–300 m, are composed of fine and small-grained sands, siltstones with intercalations of clays, limestones, and sandstones with a thickness ranging from 2–28 m. The base rocks are represented by sandy clay sediments, present throughout the upper Sarmatian-Meotian complex of the Moldovan Artesian Basin [5].

However, it's important to note that anthropic environmental pollution factors have significantly impacted water quality over recent decades. Industrial activities, such as mining and energy production, can release hazardous chemicals into the water. Agriculture also contributes to water pollution through the excessive use of fertilizers and pesticides, which seep into waterways. Urbanization and infrastructure development can lead to increased pollution with heavy metals and other pollutants. Untreated household and industrial waste can contaminate water with pathogenic bacteria and viruses, among other things. All these factors can negatively impact water quality, affecting human health and biodiversity. Therefore, the sustainable and proper

management of water resources is of utmost importance [6-8].

A significant source of natural waters, by origin, is the underground and phreatic ones that supply the population through the decentralized system (wells and springs). The quality of drinking water in the Republic of Moldova is subpar, with the situation being more severe in rural localities where wells are the main source of water. This can significantly impact the health of the population.

At present, in the Republic of Moldova, there is a network of 182 observation wells, of which 122 are in a malfunctioning state, while the remaining 60 are in a weakly malfunctioning state. However, the current monitoring network consists of 33 stations, yet these are not reflected on the pages of the State Hydrometeorological website [9]. The situation becomes even more critical when analysing groundwater quality. Data on the quality of groundwater in the Republic of Moldova are practically nonexistent [5].

According to European Union legislation, everyone has the right to quality drinking water [10]. In this regard, on December 30, 2005, by decision No. 1406, the Government of the Republic of Moldova approved a "New water supply and wastewater treatment program for the localities of the Republic of Moldova until 2015" [11]. However, even though this program was implemented, almost half of the population still does not have access to centralized water services and/or quality drinking water in 2024. This program will remain a priority and will be maintained for many years to come until responsible authorities develop water distribution networks throughout the country, ensuring citizens' needs, including public fountains and springs, as well as monitoring and preventing water source pollution.

An example of a locality in the Republic of Moldova is the village of Cișmea, located in the Orhei district. Its coordinates are 47°24'56.0"N 28°45'05.9"E and it is in the immediate vicinity of the main road M2/R6 [12]. Upon accessing the State Hydrometeorological site, it was observed that it does not contain data about the water quality in the wells of the villages of the Republic, including in the locality of Cișmea [9]. Furthermore, the water quality could not be verified at the local authorities in the village because there does not possess any monitoring documents on the quality and chemical composition of the water in the local area, which should be provided by a nationally recognized health and hygiene organization. Since specific information about the chemical composition of water in the village of Cișmea in the Republic of Moldova is missing, this study remains relevant and practically significant, as it directly or indirectly impacts the health of the population in the Republic of Moldova.

Each metal can be characterized by an Anthropogenic Disturbance Factor (ADF), defined as the ratio between the annual global natural inputs (natural factors, water contact with rocks) and the inputs due to human activities (anthropogenic factors, pollution). These, along with the toxicity potential of the metal, are important factors in choosing the metals that need to be studied. Pb, Cd, Cu, and Zn have the highest ADFs. The element Cr also has a superunitary ADF, but it is among the least toxic heavy metal. The most toxic effects manifest compounds of Cd, Hg, and Pb elements. Although compounds of Hg have an estimated ADF of only 0.8, and its anthropogenic inputs currently have a decreasing trend as a result of restrictions in use, Hg is considered a metal of primary ecotoxicological importance [6,13-17]. Therefore, it was decided to conduct an investigation that will include a verification of compliance with the current standards and regulations of water quality and if there is pollution, then these analysis data will identify the sources of pollution, as well as specify the concentrations of chemical elements, heavy elements, toxic or trace elements in the migration processes in the hydrological aquatic basin of the locality.

The aim of this study was to determine pH, conductivity, hardness, chloride and sulphate content, and the concentrations of chemical elements in water samples using the ICP-OES method, complemented by physico-chemical and organoleptic methods. The study aims to provide a detailed assessment of the chemical parameters of water, identifying both essential and potentially toxic elements, in order to better understand the chemical composition of water in the village of Cișmea, located in the Orhei district of the Republic of Moldova.

Experimental

Materials

Sodium disubstituted ethylenediamine tetraacetate (Na_2H_2EDTA), silver nitrate ($AgNO_3$), potassium chromate (K_2CrO_4), barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$), hydrochloric (HCl), nitric (HNO_3) and hydrofluoric (HF) acids with qualifiers ACS reagent were procured from Ecochimie SRL (Moldova). The argon qualifier as pure for spectrometry (99.995%) was purchased from Linde Group (România).

The hydrochloric, nitric and hydrofluoric acids, used in digestion, were purified using the "distillacid BSB-939-IR" device (Berghof), which is a "subboiling" type purifier, and the distillates corresponded to the "ultrapure" qualifier. As primary standard solutions, were used reference materials sourced from Merck, Sigma-Aldrich, and Supelco® with qualifiers "certified reference material TraceCERT®". Additional details about authentic reference standards and the internal standard (IS) can be found in Tables S1 and S2 (in the Supporting Information). The preparation of calibration solutions involved using the aforementioned standard solutions and class A-rated glassware from ISOLAB and BRAND, along with adjustable volume pipettes.

The deionized water used, with a resistivity of 18.2 MΩ/cm, was produced in accordance with ISO 3696 principles of reverse osmosis at the Simplicity UV equipment (Merck Millipore) and corresponds to the "ultrapure" qualifier [18,19].

Sampling points description

To achieve the objectives of this study, water samples were collected from wells and springs in various areas of the Cișmea locality, as well as from the nearby Răut River (Table 1 and Figure 1). Thus, water samples were collected: from the northeast side of the village, samples 3 and 6; from the middle area of the village, samples 4 and 5; and from a well near the main road M2/R6, sample 2.

The methods used for water sampling were based on the water sampling standards in accordance with current legislation and ISO 5667 [20]. To be representative, multiple sub-samples of water from springs and wells at different depths in the aquifer were collected, which were later combined to form a composite sample. The water sample from the Răut River included the collection of multiple sub-samples at different downstream flow times of the river water [21]. The water sample from the water supply network was collected after the tap was opened and the water was allowed to flow at maximum pressure for 15 minutes. Subsequently, the representative samples were stored in hermetically sealed plastic containers and transported to the laboratory [18,22].

Table 1

Coordinates for water sample collection in the Cișmea locality.

Sample	*Source of samples*	*Data of sampling*	*Coordinates*
1.	Răut River	15.10.2023	47°22'59.1" N; 28°44'51.5" E
2.	Spring near R6/M2	15.10.2023	47°24'38.9" N; 28°45'10.5" E
3.	Tap, artesian water	15.10.2023	47°25'14.5" N; 28°45'19.9" E
4.	Spring in centre of the village	15.10.2023	47°24'54.7" N; 28°45'14.1" E
5.	Well in centre of the village	15.10.2023	47°24'48.6" N; 28°45'16.1" E
6.	Well, the furthest from R6/M2	15.10.2023	47°25'11.3" N; 28°45'28.5" E

Figure 1. Map with sample collection points.

Methods

Before being subjected to analyses and acid digestion, water samples were filtered using cellulose membrane filters d< 0.45 μm.

The smell and taste of the waters were determined by traditional methods [23]. Water colour was determined by method A of ISO 7887 [24].

The results of the organoleptic analyses are presented in Table 2.

Hardness was determined titrimetrically, using a sodium disubstituted ethylenediaminetetra acetate (Na_2H_2EDTA) solution in an alkaline medium, according to [18,25]. Chlorides were determined by argentometry, with silver nitrate, according to [18,26]. Sulphates were determined gravimetrically by weighing $BaSO_4$, according to [18]. The pH and electroconductivity χ were measured at HANNA HI5521, equipped with HI1131 (pH), HI7662-W (thermocompensator) and HI76312 (χ) at a temperature of 20°C.

Water samples were subjected to acid digestion with microwaves at high temperatures and pressure, in hermetically sealed ultra-pure PTFE vessels, according to EPA3005A using SpeedWave four SW-4 (Berghof), for spectroscopy analysis [27]. After digestion, the acid solutions were evaporated in ultra-pure PFA flasks in the HotBlock SC 154 unit (Environmental Express), and then brought up to par with deionized water. Multielement spectral measurements by ICP-OES (Inductively Coupled Plasma Optical Emission spectroscopy) of Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hg, In, K, Li, Mg, Mn, Mo, Na, Ni, Pb, S, Sb, Se, Sn, Sr, Te, Ti, Tl, V, and Zn involved reading spectral emissions in *axial* and *radial* mode, at the Thermo Scientific iCAP 6200 Duo spectrometer. The iTEVA Software version 2.8.0.97 was employed for analysis. Aerosol atomization was achieved using an inductively coupled plasma torch in a continuous flow of argon at a pressure of 5 bar. Intensity readings for the analyte signals were corrected based on the percentage recoveries of the internal standard, scandium (Sc) [28]. The internal standard solution contained 5 mg(Sc)/L. Reference spectral lines for Sc at wavelengths 188.060, 227.318, 361.384, and 391.181 nm were utilized. To identify the 36 analytes of interest, it was referred to the spectral lines listed in Table S1 (in the Supporting Information). Calibration curves were developed using 15 standard solutions, covering linearity ranges from 5 μg/L to 151 mg/L, ensuring correlation coefficients (R^2) exceeding 0.95 [29]. The blank solution $HCl : HNO_3 : HF$= 2:1:0.1 (in % v/v) was used. In Table S1, was provide the coefficients of the calibration curves (a, b, and R^2), linear range domains (LN), detection limits (LD), and determination uncertainties (U).

Results and discussion

To assess the chemical composition of water in the Cișmea locality area, Orhei district, a total of 6 water samples were collected and analysed, representing 3 different types of water sources. The first water source is *surface water*, represented by sample 1. It was collected from the Răut River in close proximity to the Cișmea locality, at coordinates 47°22’59.1” N; 28°44’51.5" E. This water source meets the vital needs of both wild and domestic animals in the area. The second water source, shallow groundwater (phreatic), is represented by samples 2, 4–6. Sample 3 represents the third water source, which is actually untreated groundwater (captive) extracted from the artesian well and directed through the aqueduct in the Cișmea locality [18,22,30]. The collection of these samples was conducted to faithfully reflect the entire Cișmea locality area and the water segment of the Răut River that runs through the respective zone. The sampling coordinates are presented in Table 1.

Table 2

Organoleptic evaluation of samples: smell, taste, and colour.

Parameter	*Sample*					
	1	*2*	*3*	*4*	*5*	*6*
The character of the smell	B	Pn	N	L	N	N
Odour intensity, in degrees	3	1	2	2	2	1
The character of the taste	-	Weak	Distinct	Weak	Weak	Very weak
Taste intensity, in degrees	-	2	3	2	2	1
Colour	Weak greenish	A	A	A	A	A

Note: B - from the pond; Pn - from the earth; N - undetermined; L - from wood; A - Acceptable to consumers and no abnormal change.

The collected samples were examined for organoleptic parameters such as colour, taste, and smell, and investigated for general physico-chemical parameters including hardness, chloride content, sulphates, pH, and conductivity. Only common parameters that can be evaluated for all these types of water were chosen. Additionally, 36 chemical elements were analysed, encompassing macroelements, microelements, trace elements, toxic elements, and heavy metals. These include: Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hg, In, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Sn, Sr, Te, Ti, Tl, V, and Zn [18,31].

The odour and colour of samples were determined according to Annex 1 of the Government Decision (Republic of Moldova) No. 890 of 12.11.2013, for surface waters, [32]. The character and intensity of the odour of water sample 1 are typical of 'pond' water, and the greenish colour indicates the presence and development of organisms, likely green algae. The other samples did not deviate in terms of odour, taste, and colour indicators and were assessed as 'acceptable for consumers and without abnormal changes' (Table 2).

The results of the general physico-chemical parameters are presented in Table 3.

The pH values in these water sources range from 7.51 to 7.99, classifying them as slightly alkaline. These values fall within the range considered safe for human consumption [33]. The presence of an alkaline environment in water suggests that processes of "hydrolysis after anion" are occurring. This leads us to the conclusion that there is an increased likelihood of neutral anions such as Cl^-, SO_4^{2-}, as well as partially hydrolysed anions, especially HBO_3^{2-} and $H_2BO_3^-$, $HSiO_3^-$ and SiO_3^{2-}, HCO_3^- and CO_3^{2-}. In an alkaline environment, the probability of high-charge transition metal cations being present is significantly reduced. Instead, alkali and alkaline earth metal ions are more abundant, as most of their salts are soluble in water. Transition and post-transition metal ions are typically hydrolysed in neutral to slightly alkaline media, forming hydroxides that are sparingly soluble in water and are not toxic in these pH conditions. An exception to this rule is represented by the salts of V, Ti, Mo, and W, which form vanadate, titanate, molybdate, and tungstate anions, respectively, relatively soluble in neutral and alkaline media [1,2].

It is well known that water hardness is an important factor in assessing water quality. The determination of total hardness, which indirectly expresses the quantities of Mg^{2+} and Ca^{2+} ions present in water, is crucial because these ions directly impact human health, including the muscular, skeletal, nervous, and cardiovascular systems. The method described in ISO 6059 recommends titration with EDTA at pH 10; however, this method does not faithfully represent this parameter [34]. It does not account for the titratable amount of foreign ions, such as Sr^{2+}, Ba^{2+}, Be^{2+}, or transition metal ions like Cu, Zn, Cd, Hg, or posttransition Al, Sn, Pb, Bi, etc., which is a limitation. For these reasons, Table 3 presents two values for hardness: one determined according to ISO 6059 (column 1* - EDTA) and the other based on the sum of Mg^{2+} and Ca^{2+} ion concentrations determined by ICP-OES (column 2* - Mg^{2+}+Ca^{2+}) [31].

The hardness values for samples 1-6 fall within the normal range, ranging from 14.8 to 39.2 °dH (Table 3 and 4). However, the significant difference in these results obtained using different methods confirms the assumption that, in addition to the target ions Mg^{2+} and Ca^{2+}, there are increased quantities of titratable "foreign" ions. This assumption is further supported by the conductivity values exceeding the Maximum Allowable Concentration (MAC). For samples 2-6, the conductivity (χ) values range from 2670 to 4470 μS/cm, indicating deviations beyond the MAC. Electrical conductivity in water is directly proportional to the concentration of ions present, which can originate from salts, minerals, metals, or other soluble substances.

Table 3

Results of the investigations in samples 2-6: hardness, chloride and sulphate content, pH, and conductivity.

Parameter	*Sample*					*MAC*
	2	*3*	*4*	*5*	*6*	
Hardness (EDTA), °dH	30.2±1.5	20.2±0.9	15.7±0.7	30.0±1.3	14.8±0.6	>5*
Hardness (Ca+Mg), °dH	26.6±0.2	19.8±0.4	15.2±0.3	31.0±0.2	16.0±0.1	>5*
Conductivity χ, μS/cm	4470±9	2673±6	3530±7	3839±7	3740±7	2500
Chloride, mg(Cl^-)/L	103±1.8	47.2±0.5	51.3±0.5	88.0±0.9	55.4±0.5	250
Sulphate, mg(SO_4^{2-})/L	259±2	132±0.9	70.0±0.5	128±1	148±1.7	250
pH	7.98±0.01	7.70±0.01	7.63±0.01	7.51±0.01	7.99±0.01	6.5–9.5 #

Note: * - minimum allowed value; #- allowed range.

In the case of drinking water from various sources, the legislation in the Republic of Moldova specifies a maximum conductivity of 2500 μS/cm. The United States Environmental Protection Agency (EPA) recommends a maximum Total Dissolved Solids (TDS) of 500 mg/L, which corresponds to approximately 1000 μS/cm [2,35]. Therefore, if the water conductivity values from these sources fall between 2670 and 5400 μS/cm, it could indicate a high level of dissolved solids, exceeding the safe limit for human consumption, possibly due to pollution or naturally occurring mineral content.

For clarification, an ad-hoc determination of anions and cations was conducted for these sources. Variations were observed in the chloride and sulphate indicators for samples 2–6, although these values generally fall within legal limits or show only minor deviations. For instance, sample 2 exhibits slightly elevated chloride levels (103 mg(Cl^-)/L), which still remain within the norm. However, in the case of sulphates, with a value of 259 mg(SO_4^{2-})/L, an exceedance of the maximum allowable concentration is noted. The situation differs for the water samples from the locality. The hardness, chloride, and sulphate values are approximately half of those in samples 1.

Sample 1 shows significant exceedances for several parameters, with sulphate levels at 547 mg(SO_4^{2-})/L. Tables 5 and S3 presents the concentration values of the 36 elements determined by the ICP-OES method. The water of the Răut River is characterized by very high concentrations of Na^+, K^+, Mg^{2+} and Ca^{2+} ions, as well as transition elements (Tables 4 and S3), with magnesium at 109 mg(Mg^{2+})/L and the sum of ions (Na^++K^+) at 352 mg/L. According to [32], the water of the Răut River in the Cişmea area is classified as category V, the most polluted.

Despite efforts, a specific number of localities through which the Răut River flows in the Republic of Moldova have not been definitively identified. Upon studying the map of the Republic of Moldova, it was observed that the Răut River passes through several localities, including the larger towns of Bălți and Florești, before reaching Cișmea. From Florești, the Răut River follows its course along the R14/M2 road segment (from Soroca) until it intersects with the R6/M2 road, passing through 21 localities (such as Mărculești, Varzareuca, Bobulești, Stîrcești, Cenușa, Țîra, Rogojeni, Roșietici, *etc*.). The river continues to flow parallel to the R6/M2 road segment, traversing localities such as Sărătenii Vechi, Ciocîlteni, Feodoreuca, Mălăiești, Târzieni, Brăviceni, and Inculeț, until it reaches the locality of Cișmea. Initially, it was assumed that high concentrations of sodium (Na), magnesium (Mg), as well as lithium (Li) and sulphur (S) are largely influenced by pollution "near the road," particularly due to the excessive use of anti-skid materials during winter, compounded by the presence of an improvised construction waste dump nearby. However, according to [5], the aquifer in the Cișmea locality is associated with the Moldovan Artesian Basin (MAB), specifically with the Aluvial-Deluvial aquifer horizon (aA3), which supplies water to wells and springs (groundwater), and the Badenian-Sarmatian aquifer complex (N1b-S1), which stores underground water. Both the aA3 and N1b-S1 waters are characterized by elevated concentrations of sulphates, chlorides, and ions such as Na^+, K^+, Mg^{2+} and Ca^{2+} [30]. It was anticipated that elevated concentrations of these elements would be identified in the water sample 2. For sample 2, the sodium concentration is 401 mg(Na)/L, exceeding the MAC for drinking water by approximately 2 times. This value is even higher than that of the Răut River water, which has a sodium concentration of 334 mg(Na)/L. Sodium values for water samples 4-6 range between 276–381 mg(Na)/L, surpassing the guideline value by approximately 1.4-1.9 times. As for sample 3, the drinking water from the village aqueduct falls within the current legal limits, with a sodium concentration of 122 mg(Na)/L.

Table 4

Some parameters determined in sample 1 and MAC values for surface water.

Parameter	*MAC for category*					*Sample 1*
	I	*II*	*III*	*IV*	*V*	
Chloride Cl^-, mg/L	<80	150	250	300	>300	137±2
Sulphate, mg(SO_4^{2-})/L	<100	150	200	350	>350	547±5
Magnesium Mg^{2+}, mg/L	<40	50	60	100	>100	109±2
Calcium Ca^{2+}, mg/L	75	150	200	300	>300	91±1
Sum of ions Na^+ + K^+, mg/L	<40	55	70	100	>100	352±10
Hardness (EDTA), °dH	<22.4	33.6	50.4	84	>84	39.2±1.8
Hardness (Ca+Mg), °dH						37.7±0.5
Conductivity χ, μS/cm	-	-	-	-	-	5400±10
pH	6.5÷8.5	6.5÷9.0	6.5÷9.0	6.5÷9.0	<6.5 or >9.0	8.42±0.01

Besides all of this, the water from samples 2, 4–6 contains high levels of boron, ranging from 0.8 to 1.65 mg(B)/L, which exceeds the recommended MAC for drinking water by approximately 1.6-3.3 times. Only sample 3, with 0.33 mg(B)/L, falls within regulatory limits. Sample 1, representing surface water from the Răut River, contains 0.92 mg(B)/L (Table S3), but according to sources [32,36], this parameter is not regulated for surface water.

For drinking water, there are no specific regulations regarding the content of strontium (Sr) and barium (Ba) according to current legislation [10,33]. In the Union of Soviet Socialist Republics, strontium levels were regulated, and they were not supposed to exceed 7 mg(Sr)/L [37]. In the United States of America, the Environmental Protection Agency (EPA) has established a health-based screening level for strontium in drinking water at 4.0 mg(Sr)/L [38]. This level is not a regulation but rather a guideline for assessing potential health risks. Notably, the highest strontium concentration, 8.24 mg(Sr)/L, is found in water sample 3, which is actually groundwater. Compared with GOST or EPA standards, the water from the Cișmea locality's aqueduct has a higher strontium concentration than the presented norms. As a chemical element related to calcium, strontium (Sr) significantly impacts the processes of bone formation and bone turnover in living organisms. It can influence bone tissue resilience.

Table 5

Elemental composition of samples 2−6 analysed using ICP-OES.

No.	*Element*	*Sample / Concentration*					*MAC*	*Unit of measure*
		2	*3*	*4*	*5*	*6*		
1.	Ag	20.9±0.4	20.7±1.1	18.3±6.6	16.4±1.3	16.8±0.2	-	µg/L
2.	Al	80±5	80±3	65±2	96±10	90±15	200	µg/L
3.	As	19.6±0.7	17.4±1.9	19.2±1.3	17.3±1.3	17.3±0.6	10	µg/L
4.	B	1.65±0.03	0.33±0.03	1.08±0.04	1.06±0.01	0.80±0.04	0.5	mg/L
5.	Ba	0.088±0.010	0.072±0.007	0.087±0.002	0.096±0.005	0.090±0.007	-	mg/L
6.	Be	<8.7	<8.7	<8.7	<8.7	<8.7	-	µg/L
7.	Bi	22±0.9	18±0.2	20±0.6	25±3.0	22±0.5	-	µg/L
8.	Ca	48±0.3	48±0.3	38±1.2	69±0.5	31±0.14	-	mg/L
9.	Cd	10.5±0.1	10.5±0.1	10.5±0.1	10.5±0.1	10.5±0.02	3	µg/L
10.	Co	11±0.3	10±0.1	11±0.1	11±0.1	11±0.14	-	µg/L
11.	Cr	9.2±2.4	7.1±3.1	23.3±1.9	23.9±3.0	39.2±2.5	50	µg/L
12.	Cu	0.013±0.004	0.011±0.001	0.011±0.001	0.010±0.001	0.011±0.001	1	mg/L
13.	Fe	<0.005	<0.005	<0.005	<0.005	<0.005	0.2	mg/L
14.	Ga	37±2	47±9.9	<29.5	40±15	33±11	-	µg/L
15.	Ge	<20	<20	<20	<20	<20	-	µg/L
16.	Hg	<0.5	<0.5	<0.5	<0.5	<0.5	1	µg/L
17.	In	13±0.1	11±1.8	12±0.2	12±0.6	13±1.0	-	µg/L
18.	K	7.6±0.2	12.0±0.13	11.3±0.5	22.3±0.8	4.7±0.12	-	mg/L
19.	Li	0.139±0.005	0.066±0.002	0.063±0.001	0.080±0.008	0.086±0.003	-	mg/L
20.	Mg	86.4±0.7	57.1±1.5	43.2±0.4	92.9±0.5	50.8±0.06	-	mg/L
21.	Mn	24±1.0	29±0.8	19±0.4	19±0.1	22±0.3	50	µg/L
22.	Mo	2.0±0.1	0.5±0.1	2.3±0.1	1.3±0.2	1.50±0.01	-	µg/L
23.	Na	401±8.0	122±0.8	276±9.9	332±10	381±7.6	200	mg/L
24.	Ni	12.5±0.1	12.6±0.3	10.8±0.2	10.9±0.1	10.3±0.1	20	µg/L
25.	P	4±1.3	6±3	105±2	64±1	15±3	-	µg/L
26.	Pb	18.7±0.3	22.5±0.1	16.5±0.1	17.2±0.3	15.6±0.4	10	µg/L
27.	S	115±1.4	87±0.5	31±0.5	70±1.4	75±0.13	-	mg/L
28.	Sb	<1	<1	<1	<1	<1	5	µg/L
29.	Se	4.4±0.8	<1.4	7.5±0.6	4.3±0.1	3.4±0.9	10	µg/L
30.	Sn	9±0.1	5±0.1	8±0.1	9±0.2	9±0.4	-	µg/L
31.	Sr	1.60±0.01	8.24±0.04	0.74±0.01	1.47±0.01	0.83±0.01	-	mg/L
32.	Te	11±0.6	11±0.6	11±1.1	12±1.0	11±0.3	-	µg/L
33.	Ti	<3.1	<3.1	<3.1	<3.1	<3.1	-	µg/L
34.	Tl	7±0.6	10±1.5	7±1.3	7±0.3	7±0.9	-	µg/L
35.	V	9±0.2	8±2	10±0.8	8±3	7±2		µg/L
36.	Zn	10.6±0.1	12.4±0.1	11.1±0.1	14.1±0.2	23.4±0.5	3000	µg/L

Studies suggest that strontium absorption may be suboptimal in women with osteoporosis. However, it's essential to remember that strontium can also have a negative impact on bone health. For instance, replacing dietary calcium with strontium has been associated with reduced bone mineralization and inhibition of intestinal calcium absorption.

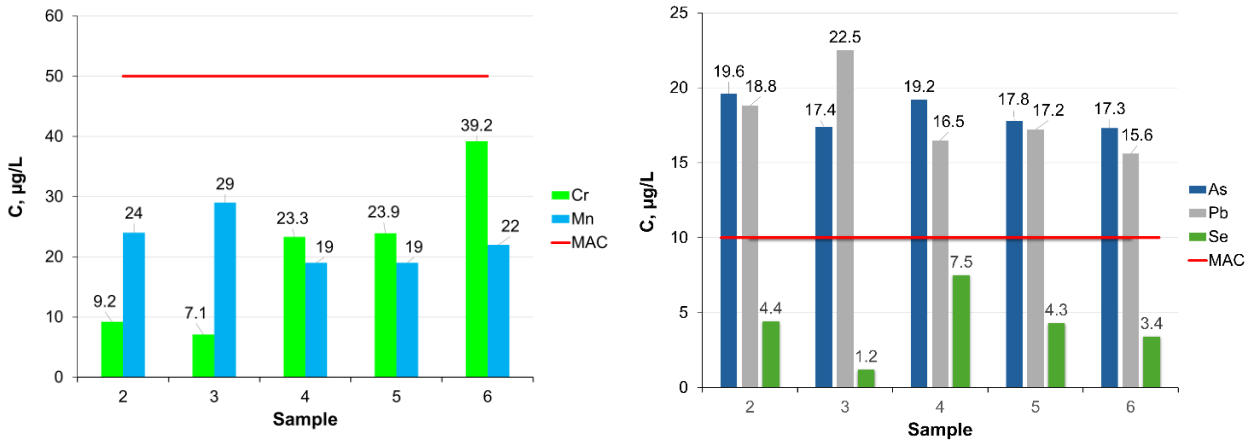
By comparing the strontium value of 4.24 mg(Sr)/L in sample 1 (Table S3) with the range of 0.74–1.60 mg(Sr)/L in the other samples, we can assess the degree of pollution in the Răut River water. Considering that this river is a surface water source, it should not have a strontium concentration of 4.24 mg(Sr)/L. In contrast, strontium levels in the Dniester River water fluctuate seasonally within the range of 0.4–0.8 mg(Sr)/L.

For none of the six water samples collected, deviations in the regulated parameters of manganese (Mn) and chromium (Cr) are observed. In sample 1 from the Răut River, concentrations of 18 µg(Mn)/L and 6.3 µg(Cr)/L were identified (Table S3). Sample 2, located near the R6/M2 road, exhibited values of 24 µg(Mn)/L and 9.2 µg(Cr)/L. For the local spring-fed wells (samples 4–6), manganese concentrations ranged from 23.3 to 39.2 µg(Mn)/L, and chromium concentrations ranged from 19 to 22 µg(Cr)/L. As for the water from the village aqueduct (sample 3), it contained 29 µg(Mn)/L and 7.1 µg(Cr)/L, without notable deviations in these parameters (Figure 2*(a)*).

It is observed that the MACs are exceeded for arsenic and lead, but not for selenium (Figure 2*(b)*). The selenium concentration in the Răut River water sample is 3.9 µg(Se)/L, a value comparable to that in the Dniester River, which is around 3.0 µg(Se)/L [39]. The lowest selenium concentration was found in the aqueduct water (sample 3), which is groundwater, with a value of 1.2 µg(Se)/L. Conversely, the highest concentration was in the spring water from the village centre (sample 4). As for arsenic, all samples exceed the MACs, including surface water, groundwater, and aqueduct water (subterranean). The largest exceedances were recorded in the Răut River sample (19.1 µg(As)/L), sample 2 (19.6 µg(As)/L), and sample 3, the aqueduct water (19.2 µg(As)/L). The village wells have arsenic values ranging from 17.3 to 17.8 µg(As)/L, which means they exceed the MACs by 1.73–1.96 times.

It was assumed that lead concentrations would exceed the MAC in the water sample from the Răut River, given its immediate proximity to the R6/M2 road. However, in this series of deviations, sample 1 presents the lowest value that surpasses the MAC, with a lead content of 12.2 µg(Pb)/L, which is an excess of 1.2 times. Sample 2, representing spring water located 'near the road', has a concentration of 18.8 µg(Pb)/L, approximately 1.9 times higher than the MAC. The village wells and spring (samples 4–6) recorded deviations ranging from 1.56 to 1.72 times above the MAC (Figure 2*(b)*). The highest deviation from the MAC was observed in the aqueduct water (sample 3), with a lead concentration of 22.5 µg(Pb)/L, approximately 2.2 times the MAC. We currently lack an explanation for such elevated levels of this element in the tap water (extracted from the local artesian well).

Cadmium, a heavy metal, can be found in elevated concentrations in both drinking water and surface water due to industrial pollution. Exposure to high levels of cadmium can have detrimental effects on health.



(a) *(b)*

Figure 2. MAC values and concentrations of microelements Mn and Cr *(a)* and toxic elements As, Pb, and Se *(b)*, in µg/L, in water samples 2–6.

Consuming water contaminated with cadmium can lead to its accumulation in the body, potentially causing kidney and bone issues. Moreover, cadmium is classified as a human carcinogen and may increase the risk of lung cancer. It is crucial to closely monitor and regulate cadmium levels in the local water supply to protect citizens' well-being. The cadmium concentration values in the analysed samples are approximately 10.5 µg(Cd)/L, which exceeds the MAC by about 3.5 times.

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The concentrations of the elements bismuth (Bi), thallium (Tl), and vanadium (V), expressed in µg/L, in samples 1 to 6 are illustrated in Figure 3. It is important to note that, according to European and Moldovan legislation, there are no established standards for the levels of these elements, including different types of water – surface water and water from underground sources. Bismuth concentration values range from 16 to 25 µg(Bi)/L. The lowest concentration is found in sample 1. The highest bismuth concentration is observed in sample 5 (Figure 1 and 3). As for thallium, the lowest concentration is in sample 2, situated 'near the road' with a value of 7 µg(Tl)/L. The highest thallium concentration is in the village aqueduct (sample 3), with a value of 10 µg(Tl)/L.

Thallium occurs naturally in low concentrations in the environment. The most common sources of thallium pollution are atmospheric emissions and depositions from industrial activities, particularly in areas where sulphide ores have been processed or near coal-fired power plants, brick factories, and cement production sites. Between 1950 and 1970, compounds containing thallium were widely used in the Soviet Union as rodenticides. The most commonly used compound was thallium sulphate (Tl_2SO_4), which is colourless, odourless, and tasteless [40-42]. The fact that sample 2 has the lowest thallium concentration can be explained by its relative distance from human settlements and treated agricultural fields.

The concentrations of vanadium in the collected water samples are approximately 7–9 µg(V)/L (Figure 3).

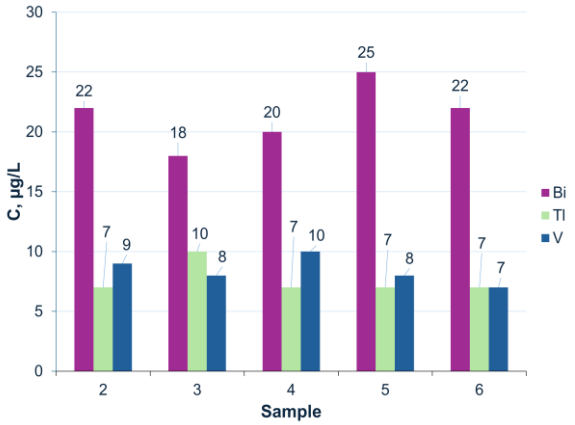

Figure 3. Illustration of the concentrations of the elements bismuth, thallium, and vanadium, in µg/L, in water samples 1 to 6.

Conclusions

Analyses were conducted on three types of water in the locality of Cișmea, a village situated near the M2/R6 main road, at coordinates 47°24'56.0"N 28°45'05.9"E. The analysed water types included surface water, groundwater collected from springs and wells, as well as water sourced from the aqueduct, which is groundwater from the local artesian well.

To determine the qualitative and quantitative characteristics of these waters, a series of methods were employed. These methods encompassed organoleptic assessments (smell, taste, colour), physical measurements (pH and electrical conductivity), and chemical analyses (gravimetry and titrimetry for hardness determination, sulphate and chloride content). Levels of 36 chemical elements were determined using the ICP-OES method.

The water hardness in the locality of Cișmea ranges from 8.1 to 19.9 °dH, which falls within normal limits (values greater than 5 °dH). This hardness is consistent with electrical conductivity levels (χ) in the range of 2670–5400 µS/cm, indicating the presence of a high concentration of dissolved solids. These characteristics are specific to the Cișmea aquifer, which belongs to the Aluvial-Deluvial aquifer horizon (aA3) and the Badenian-Sarmatian aquifer complex (N1b-S1).

All samples present significant deviations from the MAC values for the parameters determined by the ICP-OES method. All samples exhibit significant deviations from the MAC

values for arsenic. Concentrations range between 17.3 and 19.6 μg(As)/L, exceeding the MAC by 1.73 to 1.96 times. For lead, the values span from 12.2 to 22.5 μg(Pb)/L, surpassing the MAC by 1.2 to 2.2 times. Notably, tap water registers the highest lead level. Cadmium levels reach approximately 10.5 μg(Cd)/L, exceeding the MAC limits by more than 3.5 times. Sample 3, sourced from the artesian well in the locality, contains strontium concentrations of 8.24 mg(Sr)/L. This value is approximately 2.1 times higher than the EPA (USA) norms.

The concentrations of barium, bismuth and thallium are not regulated by European or Moldovan legislation. Barium level range from 0.072 to 0.096 mg(Ba)/L. Bismuth levels range from 16 to 25 μg(Bi)/L, while thallium levels are between 7 and 10 μg(Tl)/L. The water from the village's aqueduct has the highest thallium concentration. No deviations observed for Al, Cr, Cu, Fe, Hg, Mn, Ni, Sb, Se and Zn.

None of the five sources of drinking water comply with current legislation and all show significant deviations from potable water requirements. The water from the Răut River, in the Cișmea area, falls into pollution category V (the most polluted) and poses an increased risk to animals.

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Supplementary information

Supplementary data are available free of charge at http://cjm.ichem.md as PDF file.

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