Evaluation of the Chemical Composition of Drinking Water from Different Sources

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This study evaluated the chemical quality of drinking water from 157 sources across northern, central, and southern regions of the Republic of Moldova, sampled during two seasonal campaigns. Significant differences were observed between source types, with wells showing the highest contamination levels: 35.7% of samples exceeded the nitrate limit (50 mg/L), 33.1% exceeded the sulfate limit (250 mg/L), and 23.6% surpassed the TDS threshold (1500 mg/L). Artesian boreholes frequently exhibited elevated fluoride and sulfate concentrations linked to geological formations, while public supply and filtered water were largely compliant. Statistical analysis using non-parametric tests and Principal Component Analysis (PCA) confirmed distinct hydrochemical regimes and a clear mineralization gradient across sources. These findings highlight potential public health risks, especially for rural populations relying on decentralized sources. The study underscores the need for regular monitoring and improved management of groundwater resources, although its cross-sectional design and lack of geospatial data limit the ability to assess temporal or spatial trends.

Introduction

The quality of drinking water is an essential determinant of public health, directly influencing the incidence of waterborne diseases, metabolic disorders, and chronic exposure to toxic chemical substances. According to the World Health Organization, water intended for human consumption must be free from pathogenic agents and chemical contaminants at concentrations that could adversely affect health, while maintaining an appropriate mineral balance for the body [1].

Although the present study does not directly assess health outcomes, the chemical contaminants investigated are closely linked to documented public health effects in the Republic of Moldova. Previous national reports indicate that sporadic cases of infant methemoglobinemia continue to occur in rural communities where well water contains elevated nitrate

concentrations, particularly in villages without adequate sanitation infrastructure [2]. Furthermore, several Moldovan studies have identified a high prevalence of dental fluorosis among children living in areas supplied by deep aquifers with naturally elevated fluoride levels, highlighting the long-term health relevance of hydrogeological conditions in central and northern regions of the country [3, 4]. In areas where groundwater is highly mineralized, population surveys have also reported digestive disturbances associated with increased sulfate and total dissolved solids content in drinking water, particularly in localities relying on artesian wells [5]. These epidemiological observations underline the importance of monitoring decentralized drinking water sources and justify the need for chemical surveillance studies such as the present one.

Fluoride, although beneficial in small amounts for tooth mineralization, becomes toxic at concentrations exceeding the regulatory limit, being associated with dental fluorosis and skeletal fluorosis [3, 4]. Its distribution in groundwater depends on the geological composition of the aquifer, particularly on the presence of fluoride-bearing minerals (fluorite, fluorapatite), and is frequently encountered in deep aquifers or regions with volcanic rock formations [6, 7].

Sulfates, at high concentrations, can affect the taste of water and cause digestive disturbances, serving as indicators of natural mineralization or industrial contamination. Elevated levels of sulfate, chloride, and TDS (total dissolved solids) have been reported in deep aquifers of the Republic of Moldova, resulting from the dissolution of gypsum and dolomitic minerals [8, 9].

In the Republic of Moldova, a significant proportion of the rural population relies on decentralized water sources such as wells, springs, and artesian boreholes, where quality monitoring is limited and treatment infrastructure is often lacking [10, 11]. National studies have highlighted frequent exceedances of the maximum admissible concentrations of nitrates, fluoride, and sulfates in individual drinking water sources, particularly in lowland regions and within the Dniester River basin. Recent national surveillance data provide a more detailed picture of the chemical contamination profile of decentralized drinking water sources in the Republic of Moldova. According to the Annual Report of the National Agency for Public Health (2023) [12], 62% of samples from public artesian boreholes were non-compliant for at least one chemical parameter in 2023 (compared to 72% in 2022 and 71% in 2021). Although exceedances of the nitrate limit (50 mg/L) were relatively infrequent in public boreholes (3.1% in 2023), fluoride non-compliance remained substantial (16% in 2023), reflecting the strong geochemical influence of local aquifer formations.

In contrast, individual wells and other decentralized rural sources show markedly higher nitrate contamination, with 56-60% of samples exceeding 50 mg/L NO_3^- during 2021 - 2023, and over 70% of all tested samples being non-compliant for at least one chemical indicator. These findings are attributed to both geological factors and significant anthropogenic pressures, including inadequate sanitation, improper placement of animal waste, and infiltration of domestic pollutants into shallow groundwater.

Seasonal and climatic variability is known to significantly influence the chemical composition of groundwater, particularly in temperate European regions. Changes in precipitation patterns, temperature fluctuations, and groundwater recharge affect dilution processes, mineral dissolution, and the leaching of agricultural contaminants into shallow aquifers. During dry periods, reduced recharge and enhanced evapoconcentration may lead to increased mineralization and higher concentrations of sulfates, chlorides, and total dissolved solids, whereas periods of intense rainfall promote the rapid infiltration of nitrates from agricultural soils. Evidence from Mediterranean aquifers demonstrates that climate-driven hydrological fluctuations strongly modify nitrate dynamics and salinity levels in groundwater [13]. A recent European review further highlights that climate change is expected to intensify seasonal variability in water quality, altering both the concentration and mobility of key chemical indicators [14]. These climate-driven changes in groundwater chemistry have important implications for water management, requiring more frequent monitoring during high-risk seasons, adaptive treatment strategies to manage fluctuations in mineralization and nitrate loads, and the integration of climate-resilience planning into national and regional drinking water programs.

The spatial variations observed in nitrate levels, mineralization, sulfate content, and fluoride concentrations are consistent with the hydrogeological structure of the Republic of Moldova. Shallow unconfined Quaternary aquifers, which dominate rural areas and are composed mainly of sandy and loamy deposits, have minimal protective cover and therefore show high vulnerability to agricultural and domestic pollution. National hydrogeological assessments indicate that these aquifers are the primary sources supplying wells and springs, explaining the elevated nitrate concentrations frequently documented in decentralized water sources [12, 15]. In contrast, artesian boreholes generally exploit deeper Sarmatian aquifers formed within limestone, marl, gypsum, and dolomite layers, where prolonged water–rock interaction naturally increases concentrations of sulfates, chlorides, and fluoride. Moldovan geologic surveys confirm that Sarmatian formations in the Central and Southern regions often contain gypsum-rich and carbonate strata,

which influence groundwater mineralization and fluoride levels [16]. These hydrogeological conditions explain the higher mineral content and fluoride exceedances observed in artesian water sources compared with shallow groundwater systems.

According to Directive 98/83/EC [17] on the quality of water intended for human consumption, transposed into the legislation of the Republic of Moldova, the maximum admissible concentrations are 50 mg/L for nitrates, 1.5 mg/L for fluorides, and 250 mg/L for sulfates [18]. Compliance with these limits is essential for protecting public health and preventing chronic diseases associated with exposure to chemical contaminants.

Despite the availability of national surveillance reports and several regional hydrogeochemical studies, no comprehensive comparative assessment has been conducted to evaluate the chemical composition of water from multiple source types across the Republic of Moldova using standardized analytical and multivariate approaches. Existing studies either focus on single contaminants, isolated districts, or specific aquifers, leaving a gap in understanding the overall patterns of non-compliance, the hydrogeochemical gradients that drive variability, and the relative contributions of natural versus anthropogenic factors. This study addresses this gap by providing an integrated evaluation of major ions, inorganic contaminants, and compliance rates across centralized and decentralized drinking water sources.

We hypothesized that decentralized sources (wells, boreholes, springs) would show higher non-compliance rates compared to public supply and filtered water.

Material and methods

Study design and sample collection

The study had an observational, cross-sectional design and included the analysis of a set of drinking water samples collected from different sources. Sampling covered a total of 157 drinking water sources, randomly selected from various types of water collection points used for human consumption.

To ensure representativeness, a stratified sampling strategy was applied rather than simple random selection. The sampling frame was divided into three geographical strata (Northern, Central, and Southern regions of the Republic of Moldova) and five categories of water sources (public water supply systems, wells, artesian boreholes, natural springs, and household filtration systems). Within each stratum, a list of available water sources was obtained from local public health authorities, and individual sampling points were then randomly selected using a computer-generated random number sequence. This approach ensured proportional inclusion of both urban and rural areas, as well as balanced coverage of centralized and decentralized water sources.

From each source, a representative sample was taken, for which 14 physico-chemical parameters relevant to water quality assessment were determined. The investigated sources were distributed as follows: 13 public water supply systems, 62 wells, 31 artesian boreholes, 20 natural springs, and 31 sampling points after household filtration (drinking water outlets located downstream of point-of-use domestic filtration systems installed in individual households) systems. The study covered the Northern, Central, and Southern regions of the Republic of Moldova in order to capture potential regional differences in hydrogeochemical composition and water supply infrastructure quality. Sampling campaigns were conducted in two distinct seasonal stages: October - November 2024 and March - April 2025, reflecting the climatic and hydrological conditions characteristic of the cold season and the transition to spring, respectively.

The temporal coverage of the study is limited to two sampling campaigns conducted in autumn and spring. These periods were chosen to capture transitional hydrological conditions; however, they do not encompass the full range of seasonal variability. In particular, summer months, characterized by peak agricultural activity, fertilizer application, and elevated surface runoff, and winter months, associated with reduced recharge and potential concentration of dissolved solids, were not included. As such, the results were interpreted as representative of the sampled periods rather than year-round conditions.

In this study, the term source refers to a distinct sampling point (regardless of whether the system is centralized or individual), while sample represents the analytical unit on which the 14 drinking water quality indicators were measured.

Sample collection was carried out in accordance with the standard procedures for sampling and transport established by ISO 5667-5:2006 (Water quality – Sampling – Part 5: Guidance on sampling of drinking water from treatment works and piped distribution systems).

Samples were collected in sterile polyethylene containers, previously rinsed with water from the same source, and stored at 4 °C until analysis.

Analysis of water quality parameters

For each sample, the following parameters were determined:

• General indicators: pH, total dissolved solids (TDS), total mineralization, total hardness.

• Main anions: bicarbonate (HCO_3^-), chloride (Cl^-), sulfate (SO_4^{2-}), nitrate (NO_3^-), nitrite (NO_2^-).

• Main cations: calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium + potassium.

• Other indicators: fluoride (F^-), ammonia (NH_4^+).

The determinations were carried out in accordance with international analytical standards (SM EN ISO/IEC 17025:2018) and the national methods approved for drinking water

quality monitoring. Laboratory analyses followed internationally recognized protocols, including the APHA Standard Methods for the Examination of Water and Wastewater (2017) and selected ASTM methods for water and environmental testing [19, 20], and were performed within the Chemical Testing Laboratory of the National Agency for Public Health, Republic of Moldova.

Quality assurance and quality control (QA/QC) procedures were applied throughout sampling and laboratory analysis. Field blanks and equipment blanks were collected during each sampling campaign to monitor potential contamination during sample handling and transport. Duplicate samples (10% of total samples) were taken to assess sampling and analytical precision. All laboratory analyses were performed in an ISO/IEC 17025:2018–accredited chemical testing laboratory, following validated standard operating procedures. Instruments were calibrated daily using certified reference standards, and calibration curves were verified before each analytical batch. Internal quality control samples and external proficiency testing were used to ensure accuracy, precision, and analytical reliability of the measured parameters.

Total dissolved solids (TDS) reflect the total amount of dissolved substances in water and represent the operational equivalent of the term total dry residue.

Total mineralization was calculated separately and expressed in g/L, representing the sum of all dissolved mineral salts (main ions: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-}, SO_4^{2-}), providing an overall assessment of the ionic load of the water. Although TDS and total mineralization values are closely correlated, in this study they are treated as distinct parameters, in accordance with the applied analytical methodology.

The sum of sodium and potassium (Na+ K) was determined as a composite parameter, resulting from the addition of the individual concentrations of sodium and potassium ions, expressed in mg/L. The values of each ion were also determined and reported separately to allow a detailed interpretation of the cationic composition of the water.

Method detection limits (MDLs), limits of quantification (LOQs), and analytical uncertainties were determined according to ISO/IEC 17025:2018 requirements and the validation protocols of the National Agency for Public Health Chemical Testing Laboratory. Typical MDLs for the analyzed parameters were as follows: nitrates (0.1 mg/L), nitrites (0.002 mg/L), ammonium (0.05 mg/L), fluoride (0.02 mg/L), sulfates (1 mg/L), chlorides (1 mg/L), calcium (0.1 mg/L), and magnesium (0.05 mg/L). Measurement uncertainty (expanded uncertainty, $k = 2$) ranged between ±5% and ±12% depending on the analyte and concentration range. All reported values were

above the LOQs, ensuring valid quantitative interpretation. Calibration curves, QC samples, and replicate analyses were used to verify compliance with these performance criteria for every analytical batch.

Statistical analysis

The database was compiled in Microsoft Excel and processed using SPSS version 27. For each parameter, the mean, standard deviation, minimum and maximum values, absolute and percentage non-compliance per source, and confidence intervals were calculated.

Differences between sources were tested using the Kruskal-Wallis test, and where significant differences were found, the Mann-Whitney U test with Bonferroni correction was applied for pairwise comparisons. Correlations between parameters were assessed using Spearman's correlation coefficient.

To ensure robustness and avoid overfitting in multivariate analysis, the PCA was performed on log-transformed and standardized (z-score) variables. Sampling adequacy was assessed using the Kaiser-Meyer-Olkin (KMO) measure, and factorability was confirmed with Bartlett's test of sphericity ($p<0.001$).

Compliance criteria

The results were compared with the limit values established in (**Table 1**):

• Directive (EU) 2020/2184 on the quality of water intended for human consumption [18];

• WHO Guidelines for Drinking-water Quality (2022 edition) [21];

• National sanitary regulations of the Republic of Moldova (Government Decision No. 934/2007 / Law No. 182/2019) [22, 23].

The analysis of water samples was compared against the limits established by Directive (EU) 2020/2184, the WHO Guidelines for Drinking-water Quality, and the national regulations of the Republic of Moldova, which are largely harmonized with European standards.

Table 1. Comparative table of reference values according to Directive (EU) 2020/2184, WHO Guidelines, and the Sanitary Norms of the Republic of Moldova (largely harmonized with EU/WHO standards) [18, 21, 22, 23].

Parameter	EU (2020/2184)	WHO (2022)	Republic of Moldova *
pH	6.5-9.5	6.5-9.5 (recommended range)	6.5-9.5
Nitrates (NO_3^-)	50 mg/L	50 mg/L	50 mg/L
Nitrites (NO_2^-)	0.5 mg/L	0.5 mg/L	0.5 mg/L
Ammonia (NH_4^+)	0.5 mg/L (indicator)	0.5 mg/L (indicator)	0.5 mg/L
Chlorides (Cl^-)	250 mg/L (organoleptic indicator)	250 mg/L (taste)	250 mg/L
Sulfates (SO_4^{2-})	250 mg/L (organoleptic indicator)	250 mg/L (taste)	250 mg/L
Fluoride (F^-)	1.5 mg/L	1.5 mg/L	1.5 mg/L
Total dissolved solids (TDS)	–	Acceptability: 1000-1500 mg/L (taste)	~1500 mg/L (sanitarily recommended)
Total mineralization	–	Comfort threshold ~1.5 g/L	~1.5 g/L (recommended)

* The values for the Republic of Moldova are established by Law No. 182/2019 and the Sanitary Norms for Drinking Water, which are largely aligned with EU and WHO standards.

Results and discussion

The physico-chemical analysis of the water samples revealed considerable variability in the determined parameters, depending on the source of origin and local environmental conditions. The mean values, standard deviations (SD), minimum and maximum limits, as well as the 95% confidence intervals ($CI_{95\%}$), are presented in **Tables 2-6**.

Table 2. Descriptive statistics of the analyzed parameters in water samples from the public water supply system (n=12).

Parameter	Mean	SD	Minimum	Maximum	Lower $IC_{95\%}$	Upper $IC_{95\%}$
pH	8.085	0.543	7.2	9.2	7.79	8.38
Bicarbonates, mg/L	260.385	191.795	67	769	156.124	364.646
Chlorides, mg/L	42.308	39.054	7	142	21.078	63.538
Total hardness, dH	7.954	3.849	1.4	12.3	5.862	10.046
Sulfates, mg/L	85.615	68.791	11	294	48.22	123.01
Ammonia mg/L	0.183	0.199	0.1	0.79	0.075	0.291
Nitrites, mg/L	0.023	0.028	0.003	0.091	0.008	0.038
Nitrates, mg/L	4.923	3.941	0.7	15.7	2.781	7.065
Fluoride, mg/L	0.594	1.006	0.05	3.29	0.047	1.141
Total dissolved solids (TDS), mg/L	413	304.898	80	1203	247.256	578.744
Sum Na+K, mg/L	99.462	146.485	17	482	19.832	179.092
Mineralization, g/L	0.543	0.405	0.118	1.602	0.323	0.763
Calcium, mg/L	40.154	24.09	2	66	27.059	53.249
Magnesium, mg/L	10.077	3.095	5	15	8.395	11.759

Waters from public supply systems were characterized by a slightly alkaline pH (8.08±0.54) and low mineralization (0.54 g/L). The contents of bicarbonates (260 mg/L), chlorides (42 mg/L), and sulfates (86 mg/L) were moderate, with no exceedances of the permissible values.

Table 3. Descriptive statistics of the analyzed parameters in water samples from wells (n=62).

Parameter	Mean	SD	Minimum	Maximum	Lower $IC_{95\%}$	Upper $IC_{95\%}$
pH	8.16	0.508	7.3	9.2	7.845	8.475
Bicarbonates, mg/L	776.5	393.739	262	1403	532.458	1020.542
Chlorides, mg/L	217.2	172.666	34	540	110.181	324.219
Total hardness, dH	29.85	18.446	8.7	74.3	18.417	41.283
Sulfates, mg/L	380.1	223.644	48	657	241.484	518.716
Ammonia mg/L	0.1	0	0.1	0.1	0.1	0.1
Nitrites, mg/L	0.048	0.062	0.004	0.202	0.009	0.086
Nitrates, mg/L	244.27	212.502	21.6	654.6	112.56	375.98
Fluoride, mg/L	0.878	0.864	0.05	2.51	0.342	1.414
Total dissolved solids (TDS), mg/L	1863.6	918.211	503	3404	1294.487	2432.713
Sum Na+K, mg/L	501.9	332.377	127	1180	295.891	707.909
Mineralization, g/L	2.278	1.153	0.623	4.125	1.563	2.993
Calcium, mg/L	72.4	50.997	18	178	40.792	104.008
Magnesium, mg/L	85.4	72.473	19	278	40.481	130.319

In contrast, well water showed significantly higher concentrations for all inorganic indicators, with an average mineralization of 2.28±1.15 g/L and a hardness of 29.9 °dH, indicating highly mineralized and hard water. Nitrate levels (244 mg/L) exceeded the recommended limits for drinking water, suggesting possible anthropogenic contamination.

Table 4. Descriptive statistics of the analyzed parameters in water samples from artesian boreholes (n=31).

Parameter	Mean	SD	Minimum	Maximum	Lower $IC_{95\%}$	Upper $IC_{95\%}$
pH	8.297	0.474	7.6	9.1	8.13	8.464
Bicarbonates, mg/L	641.258	237.678	244	1281	557.589	724.927
Chlorides, mg/L	70.29	69.714	9	285	45.749	94.832
Total hardness, dH	15.258	18.153	0.8	73.9	8.868	21.649
Sulfates, mg/L	404.323	444.353	17	1746	247.899	560.746
Ammonia mg/L	0.278	0.515	0.1	2.51	0.097	0.46
Nitrites, mg/L	0.634	2.056	0.003	10.706	-0.09	1.357
Nitrates, mg/L	26.716	61.208	0.7	313.8	5.169	48.263
Fluoride, mg/L	1.045	0.811	0.19	3.73	0.759	1.33
Total dissolved solids (TDS), mg/L	1291.968	841.837	486	3885	995.619	1588.317
Sum Na+K, mg/L	397.613	239.424	77	1180	313.329	481.896
Mineralization, g/L	1.624	0.943	0.672	4.722	1.292	1.956
Calcium, mg/L	45.032	49.307	2	160	27.675	62.39
Magnesium, mg/L	38.742	52.79	1	224	20.158	57.325

Samples from artesian boreholes showed a mineral composition intermediate between that of wells and springs, with an average mineralization of 1.62 g/L and a pH of 8.30±0.47. In several cases, elevated concentrations of sulfates (up to 1746 mg/L) and nitrates (313.8 mg/L) were recorded, indicating local geochemical influences.

Table 5. Descriptive statistics of the analyzed parameters in water samples from natural springs (n=20).

Parameter	Mean	SD	Minimum	Maximum	Lower $IC_{95\%}$	Upper $IC_{95\%}$
pH	7.94	0.386	7	8.7	7.771	8.109
Bicarbonates, mg/L	593.4	329.587	31	1403	448.952	737.848
Chlorides, mg/L	59.05	57.82	6	190	33.709	84.391
Total hardness, dH	21.125	10.703	0.8	40.1	16.434	25.816
Sulfates, mg/L	242.6	339.928	12	1239	93.62	391.58
Ammonia mg/L	0.348	1.009	0.01	4.63	-0.094	0.791
Nitrites, mg/L	0.018	0.031	0.003	0.123	0.004	0.032
Nitrates, mg/L	51.57	60.556	0.7	192.4	25.03	78.11
Fluoride, mg/L	1.098	1.207	0.05	4.41	0.569	1.626
Total dissolved solids (TDS), mg/L	1007.55	832.809	53	3450	642.555	1372.545
Sum Na+K, mg/L	243.35	320.06	16	1145	103.077	383.623
Mineralization, g/L	1.308	1.031	0.071	4.324	0.856	1.76
Calcium, mg/L	66.6	43.437	4	150	47.563	85.637
Magnesium, mg/L	51.15	29.493	1	111	38.224	64.076

Natural springs were characterized by a pH of 7.94±0.39, an average mineralization of 1.31 g/L, and elevated calcium (66.6 mg/L) and magnesium (51.2 mg/L) contents, values typical of bicarbonate-calcium-magnesium waters.

Table 6. Descriptive statistics of the analyzed parameters in water samples after household filtration (n=31).

Parameter	Mean	SD	Minimum	Maximum	Lower $IC_{95\%}$	Upper $IC_{95\%}$
pH	7.616	0.656	6.5	8.9	7.385	7.847
Bicarbonates, mg/L	175.194	148.859	37	683	122.791	227.596
Chlorides, mg/L	30.323	38.825	4	210	16.655	43.99
Total hardness, dH	7.587	6.562	0.3	32.2	5.277	9.897
Sulfates, mg/L	71.806	102.59	5	511	35.692	107.921
Ammonia mg/L	0.204	0.308	0.1	1.51	0.096	0.313
Nitrites, mg/L	0.009	0.013	0.003	0.063	0.005	0.014
Nitrates, mg/L	5.735	20.148	0.7	113.5	-1.357	12.828
Fluoride, mg/L	0.233	0.38	0.05	1.93	0.099	0.366
Total dissolved solids (TDS), mg/L	306.355	334.455	51	1519	188.618	424.092
Sum Na+K, mg/L	65.194	112.26	5	523	25.675	104.712
Mineralization, g/L	0.394	0.407	0.072	1.89	0.251	0.538
Calcium, mg/L	33.419	25.305	2	86	24.511	42.327
Magnesium, mg/L	12.65	17.068	0.05	88	6.642	18.658

Samples collected after filtration generally showed lower values for all parameters, with a marked decrease in total mineralization (0.39±0.41 g/L) and nitrate concentrations (5.7 mg/L). This confirms the effectiveness of the filtration process in reducing mineral load and dissolved inorganic substances.

Statistical analysis confirmed significant differences among the water sources (Kruskal-Wallis test, $p<0.001$ for most analyzed parameters). Post-hoc results showed that well water clearly differed from both public supply and filtered water, exhibiting much higher concentrations of nitrates, sulfates, chlorides, and total dissolved solids, indicating pronounced mineralization and possible anthropogenic influences on groundwater.

In contrast, water from public supply systems and filtered sources showed the lowest values of inorganic indicators (bicarbonates, sulfates, sodium+potassium, calcium, magnesium), characterized by an average total mineralization below 0.6 g/L and a slightly alkaline pH. These characteristics confirm the effectiveness of treatment and filtration processes in reducing mineral load and dissolved pollutants.

The results of the PCA analysis (Figure 1) support these findings, indicating that the first principal component (PC1) explains 54.6% of the total variance and describes a mineralization and salinity gradient associated with increased values of total dissolved solids, sodium and potassium ions, sulfates, chlorides, and bicarbonates.

The secondary component (PC2, 14.6%) highlights the contrast between samples rich in fluoride and with higher pH values, and those with increased calcium and magnesium content, often characteristic of deep groundwater or water originating from dolomitic formations.

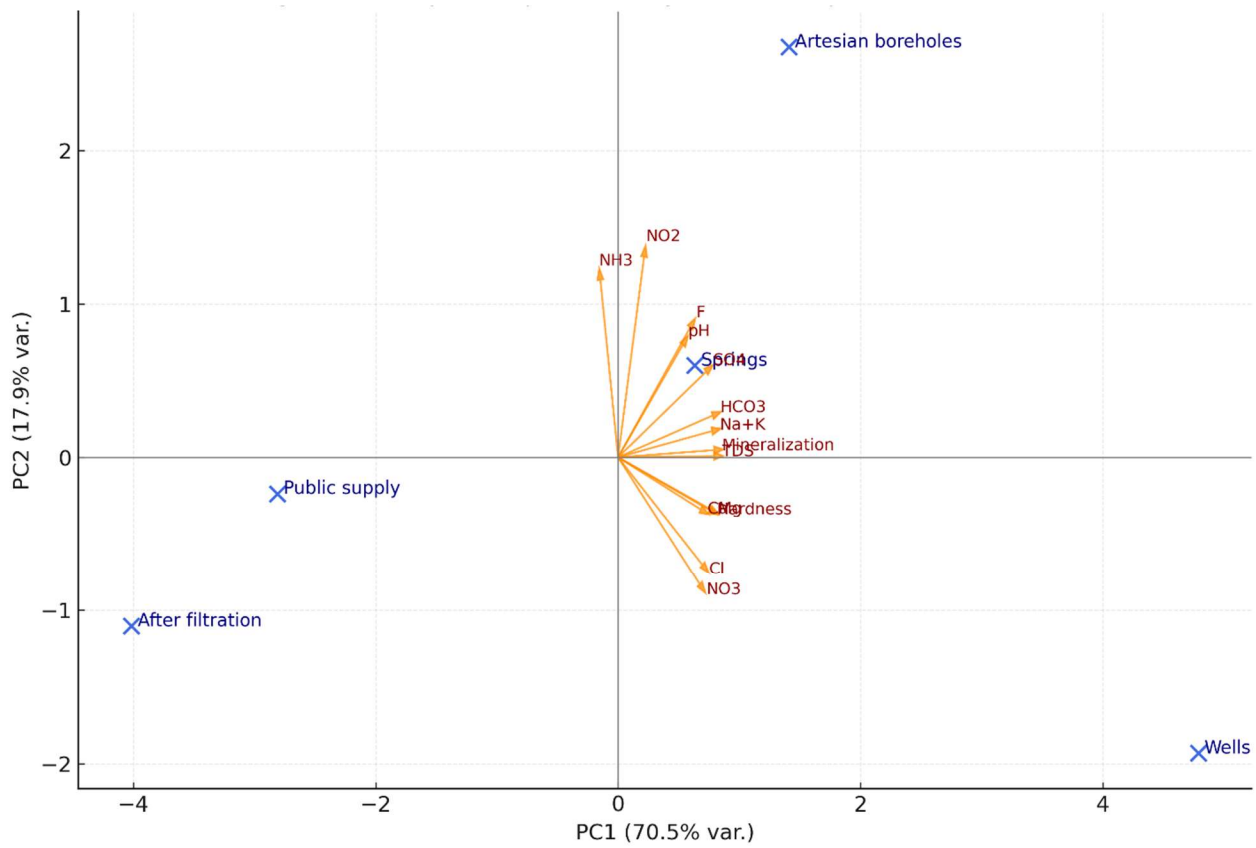

Figure 1. Principal Component Analysis (PCA) – biplot of water sources.

On the biplot diagram (Figure 1), samples from public supply systems and filtered sources cluster distinctly from those from wells and artesian boreholes, reflecting differences in geological origin and treatment level. This separation confirms the geochemical heterogeneity of groundwater and highlights the risk of sanitary non-compliance for uncontrolled sources, particularly wells and certain artesian boreholes.

The distribution of non-compliant samples by source type and parameter is presented in **Table 7**, which shows the degree of non-conformity of the analyzed water samples according to parameter and source type. Clear differences are observed between centralized and individual water sources. Water from the public supply system shows compliant values for almost all analyzed indicators, except for isolated samples exceeding the limits for sulfates, fluoride, total mineralization, and total hardness. In contrast, wells and artesian boreholes are the categories with the highest exceedances of the permissible limits. The parameters most frequently found to be non-compliant are nitrates (NO_3^-), total dissolved solids (TDS), sulfates (SO_4^{2-}), and total mineralization, with more pronounced exceedances in well water, suggesting anthropogenic contamination and higher natural mineralization of shallow groundwater. In artesian boreholes, non-conformities are mainly associated with sulfates

and fluorides, indicating geochemical influences related to the structure of the geological formations traversed. Water obtained after household filtration systems showed almost total compliance, demonstrating the effectiveness of the filtration process in reducing ionic load and dissolved substances. Natural springs fall into an intermediate category, with moderate exceedances in nitrates, fluoride, mineralization, and sulfates, but generally display an acceptable chemical profile.

Table 7. Distribution of non-compliant samples by source type and parameter.

Parameter	Unit	Public supply water, (n)	Wells, (n)	Artesian boreholes, (n)	Natural springs, (n)	After filtration, (n)	Reference value established by Law No. 182/2019	Total non-compliant, (%)
pH	-	0	0	0	0	0	6.5-9.5	0
Bicarbonates	mg/L	-	-	-	-	-	-	-
Chlorides	mg/L	0	6	2	0	0	250	5.1
Sulfates	mg/L	1	29	16	4	2	250	33.1
Ammonia	mg/L	0	1	3	1	2	0.5	4.5
Nitrites	mg/L	0	5	6	0	0	0.5	7.0
Nitrates	mg/L	0	44	4	7	1	50	35.7
Fluoride	mg/L	2	6	8	7	1	1.5	15.3
Total dissolved solids (TDS)	mg/L	0	25	8	3	1	1500	23.6
Sum Na+K	mg/L	-	-	-	-	-	-	-
Mineralization	g/L	1	38	12	5	1	1.5	36.3
Calcium	mg/L	-	-	-	-	-	-	-
Magnesium	mg/L	-	-	-	-	-	-	-
Total hardness	dH	2	1	15	2	13	minimum 5	21.0

Note: The percentage values indicate the proportion of samples exceeding the compliance limits established by Law No. 182/2019, according to the parameter and type of water source.

Directive (EU) 2020/2184, the WHO, and Law No. 182/2019 do not set limit values for hardness, Ca, Mg, hydrogen carbonates, or Na+K, as these are not considered health risk parameters.

According to the scientific literature, nitrate concentrations in groundwater from agricultural areas often exceed 50 mg/L NO_3^-. Similarly, fluoride levels above 1.5 mg/L are globally identified in calcareous aquifers or those with prolonged water-rock interaction [7]. It was demonstrated that elevated sulfate and TDS levels are correlated with long residence times in deep gravitational systems, which explains the total mineralization and “salinization” observed in wells and artesian boreholes in our study [6]. In terms of health risks, it was clearly highlighted the impact of elevated fluoride concentrations on public health [1, 3, 4, 10].

Our research shows that water from the public supply system is generally compliant, with only isolated cases of fluoride concentrations exceeding 1.5 mg/L. Well water exhibits the highest number of exceedances, particularly for nitrates (>50 mg/L, occasionally >600 mg/L), sulfates (>250 mg/L), and fluoride (>1.5 mg/L).

Water from artesian boreholes frequently shows high concentrations of sulfates and fluoride, as well as elevated total mineralization (>1.5 g/L). Spring water is highly variable, ranging from compliant sources to springs with very high levels of sulfates, fluoride, or TDS (>3000 mg/L). Water after household filtration is generally compliant for all parameters but shows very low mineralization, which may affect its taste and chemical stability.

Significant differences between the types of water sources were statistically confirmed (Kruskal-Wallis test, $p<0.001$ for most parameters), indicating the existence of distinct hydrogeochemical regimes. The principal component analysis (PCA) allowed visualization of these variations: on the biplot, samples from the public supply system and post-filtration are grouped on the left side of the graph, associated with low values of mineral ions and total dissolved solids, corresponding to treated or shallow-circulating waters. In contrast, well and artesian borehole waters are positioned on the opposite side, correlated with high contents of sulfates, chlorides, nitrates, sodium, and potassium parameters reflecting a high degree of mineralization and prolonged contact with the host rock. This distribution confirms the mineralization and salinity gradient represented by the first principal component (PC1 – 54.6% of variance), where variables with high loadings (TDS, $Na^+ + K^+$, SO_4^{2-}, Cl^-, HCO_3^-) describe the increasing trend of total mineralization from treated waters to deep groundwater. The secondary component (PC2 – 14.6%) expresses the chemical contrast between more acidic, fluoride-rich samples typical of aquifers with volcanic rocks or fluorinated sediments and harder, calcium- and magnesium-rich samples originating from carbonate formations [6, 7]. Similar results have been reported in studies from Romania, where PCA revealed the same type of separation between shallow groundwater and deep aquifers, controlled by local geology and anthropogenic influence [8, 9, 11, 24, 25].

The results presented in **Table 7** highlight significant differences among the analyzed water source types, reflecting both regional hydrogeochemical characteristics and direct anthropogenic influences. The high level of non-compliance for nitrates in well water samples suggests contamination of anthropogenic origin, caused by intensive agricultural practices, the use of nitrogen-based fertilizers, and improper management of animal waste or domestic wastewater. These trends are consistent with observations reported in numerous European and international studies, which indicate that shallow groundwater is the most vulnerable to nitrate pollution, particularly in rural areas with intensive agricultural activity [25, 26, 27].

In contrast, the elevated levels of sulfates and fluorides in water from artesian boreholes have a predominantly geological origin, associated with the dissolution of sulfate- and fluoride-bearing minerals from deep sedimentary

formations. Similar phenomena have been described in aquifers across Asia and Central Europe [6, 7], as well as in studies conducted in Romania [8], where the mineralogical composition of the substrate (gypsum, fluorapatite, dolomite) determines high sulfate and fluoride concentrations. These characteristics give artesian waters a higher total mineralization, which may exceed the compliance limits established by national and European legislation [1, 17], particularly in regions with deep aquifers.

Water from public supply systems fully meets compliance limits, confirming the efficiency of centralized treatment and monitoring systems, as well as the strict control of drinking water quality. In contrast, water from wells and springs requires periodic monitoring, as seasonal variations in groundwater level and physicochemical parameters (temperature, dissolved oxygen, flow rate) may increase the risk of exceeding maximum allowable values, particularly for nitrates and fluoride [9, 24].

The obtained results confirm the need to implement local programs for integrated water quality monitoring, with a particular focus on unprotected sources in rural areas. They also support the recommendation to educate the population on the proper use and regular maintenance of household filters as an effective measure to reduce exposure to potentially toxic substances.

Elevated nitrate concentrations in well water are consistent with known anthropogenic pressures in rural areas such as fertilizer use, livestock waste, and inadequate sanitation. National reports from the Republic of Moldova have repeatedly demonstrated strong associations between agricultural activity and nitrate contamination in shallow aquifers [12].

Limitations

A limitation of the present study is the absence of a GIS-based spatial analysis. Although regional hydrogeochemical patterns were discussed, the lack of high-resolution geolocation data for all sampling points did not allow for the development of detailed maps to visualize spatial clustering, contamination gradients, or potential hotspot areas. GIS tools are increasingly recognized as essential for identifying risk zones and supporting targeted public health interventions, particularly in countries with strong geographic variability in groundwater quality.

A further limitation of the study is the absence of a quantitative health risk assessment. Although the concentrations of contaminants such as nitrates, fluoride, and sulfates were compared with regulatory limits, no formal estimation of exposure, hazard quotients, or population-level risk was performed. Conducting a quantitative risk assessment would require additional data on water consumption patterns, demographic characteristics, and long-term exposure scenarios for the affected communities.

As such information was not available for the present dataset, the study focuses on chemical compliance rather than risk quantification.

Conclusions

The comparative analysis of physicochemical parameters across 157 drinking water sources revealed marked differences in water quality according to source type. Well water showed the highest burden of contamination, with 35.7% of samples exceeding the nitrate limit (50 mg/L), 33.1% exceeding the sulfate limit (250 mg/L), 23.6% exceeding the TDS threshold (1500 mg/L), and 36.3% surpassing the recommended total mineralization level (1.5 g/L). Artesian boreholes also demonstrated substantial geochemically driven exceedances, particularly for sulfates and fluoride. In contrast, public supply systems and household-filtered water showed near-complete compliance, confirming the effectiveness of centralized treatment and point-of-use filtration. The PCA results further supported these patterns by illustrating a clear hydrogeochemical gradient ranging from low-mineralized treated waters to highly mineralized groundwater with elevated hardness.

These findings have direct implications for public health, given the association between high nitrate levels and methemoglobinemia, excessive fluoride and dental fluorosis, and elevated TDS/sulfates and gastrointestinal disturbances. Strengthening routine monitoring of decentralized sources, especially wells and artesian boreholes, is essential to reduce exposure to chemical contaminants.

From a policy perspective, the results support the need to:

(1) expand regional monitoring programs for private wells,

(2) improve sanitation infrastructure in rural areas to reduce nitrate infiltration,

(3) provide guidance to households on the appropriate use and maintenance of point-of-use filtration devices, and

(4) integrate water quality data into regional climate resilience and groundwater protection strategies.

Future research should incorporate multi-seasonal sampling, GIS-based mapping to identify contamination hotspots, and broadened analytical scope including microbiological parameters, heavy metals, and pesticides. Coupling hydrochemical monitoring with hydrogeological mapping and land-use data will enable more robust predictive models and cumulative risk assessments.

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