

**STUDY REGARDING GROUNDWATER POLLUTION IN THE AREA
OF ȘIMNICU DE SUS**

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ABSTRACT

The purpose of the present study is to determine the degree of pollution of groundwater that supply the existing public wells in the area of Șimnicu de Sus commune. In order to achieve this objective, in the period March-May of 2023, water samples were taken from 5 wells located on the public domain of Șimnicu de Sus, Dolj county, in order to determine the degree of groundwater pollution. The water samples were collected directly from the water of the wells and were transported to the laboratory where they were subjected to the following physico-chemical determinations: pH, conductivity, total hardness, fixed residue, ammoniacal nitrogen, calcium, magnesium, nitrates and nitrites.

INTRODUCTION

Water is an essential component of the environment with profound implications in the emergence and support of life in a given area (Water Framework Directive 2000). The analysis of groundwater quality is a special necessity, which emerges from the summation of the functions performed by groundwater in its genesis, evolution and dynamics. Groundwater pollution is, for the most part, an effect of human pressure on the environment (Herman 2009, Romocea et al. 2018).

The European Union and its Member States have implemented policies and measures to improve water quality, reduce pollution and improve the condition of aquatic ecosystems.

Although groundwater is not visible, it is an essential component of the water cycle. More than 95% of the planet's fresh water, excluding glaciers and ice sheets, is underground. Groundwater provides the steady base flow of rivers and wetlands. Maintaining this flow and protecting it from pollution is essential for surface aquatic ecosystems.

Therefore one of the most important directions of development of European Union Drafts include the promotion of new and clean technologies (Savescu et al. 2010).

Groundwater is also an essential source of drinking water, supplying the hydrological systems used by 3 out of 4 EU citizens.

Groundwater is an important resource for public consumption. It can be polluted by natural sources or by human activities, the latter being the main cause of pollution, mainly from agriculture (nitrates, ammonium, etc.) (Foster et al. 2013).

One important factor contributing to the impairment of surface water quality is the use of chemical and organic fertilizers, which through runoff or leaching in water table can cause the phenomenon of pollution of surface waters and groundwater. In a river basin, the factors that determine the nutrient loads are: industry, urban sewage, atmospheric deposition, agriculture and natural system (Dodocioiu et al. 2017).

Groundwater can also represent a source of irrigation for vines, but this must comply with certain requirements in order not to harm the vines and not to contribute to the degradation of the soil through salinization (Costea 2006).

Groundwater presents a high risk of pollution, which can be reached by the fact that they can no longer constitute sources of water supply for the population, agriculture, etc. without complying with the rules of the Water Framework Directive (Dodocioiu & Buzatu 2017).

Elevated levels of nitrates in drinking water can lead to diseases such as methemoglobinemia, miscarriages, diabetes, thyroid disorders and stomach cancer (WHO, 2011). In addition to fertilizer application, the livestock, dairy and poultry sectors are also major contributors to high nitrate concentrations in groundwater (Drewry et al. 2006). Assessment of groundwater pollution could provide an important scientific basis for groundwater protection, pollution prevention and control; for this purpose, a four-step hierarchy method was constructed and applied by Zhu et al. (2018). Investigation of hydro-chemical interactions and quality of groundwater resources is essential for monitoring and identifying sources of water pollutants (Emenike et al. 2018).

Lacroix et al. (2007) show that by taking into account the heterogeneity of nitrate pollution due to soil characteristics, climate variability and agricultural contexts, a substantial part of the differences in abatement costs can be explained. Water pollution from agriculture has associated costs in terms of pollutant removal from drinking water sources, as well as damage to ecosystems, commercial fisheries, and recreational and cultural values associated with rivers, lakes, and groundwater (Parris 2011).

In order to improve environmental conditions, the development of effective strategies to mitigate nitrogen pollution has become very important. Thus, farmers were asked to change their agricultural practices, and at the level of the European Union, the best example of these pressures on farmers to redirect agriculture towards sustainability was the Nitrates Directive (91/676/EC) (Izcarra Palacios 1998; Kunkel et al. 2010) and subsequently the Water Framework Directive (2000/60/EC), both aiming to reduce water pollution by nitrate leaching from agricultural sources and to prevent further pollution through a series of measures (Velthof et al. 2014).

MATERIAL AND METHODS

The purpose of the present study is to determine the degree of pollution of groundwater from existing public wells in the area of Șimnicu de Sus commune. In order to achieve this objective, in the period March-May of 2023, water samples were taken from 5 wells located on the public domain of Șimnicu de Sus, Dolj county, in order to determine the degree of groundwater pollution.

The Șimnicu de Sus commune is located in the Șimnic terrace, within the Jiului Plain, in the temperate climate area with small influences of the Mediterranean regime. The soil consists of brown-reddish clay, good soil for agriculture and covers most of the commune. In the N-E part the soil is calcareous, washed by water and less suitable for agriculture. In the extreme N-W, the land is clayey, sandy and produces poor crops.

On the territory of the commune flows from N to S the Amaradia river which flows into the Jiu river, close to the border of Șimnicu de Sus with the village of Troaca. In spring, numerous streams flow from the eastern hills of the commune, which are formed from rainwater and snow. In recent years the courses of these streams have been drained and concreted right on their way to Amaradia. The only one that has its own spring is Șimnic or Monastery stream. It springs from the eastern part of the commune between the hills and flows westward past Jieni village, crosses Amaradia road, passes through the middle of Albești village and flows into Amaradia at the edge of Albești village. In dry weather, the flow of this stream decreases or even dries up.

The water samples were collected directly from the water of the wells subjected to this study in clean 500 ml polyethylene bottles, fitted with a screw cap in accordance with the recommendations of the specific analysis procedures. Then the place, date and time of sampling were recorded on the label of each sample bottle and the sample bottles were transported to the laboratory where they were subjected to the following physico-chemical determinations: pH by the potentiometric method, conductivity - direct determination, with the help of a suitable instrument - conductometer, total hardness, fixed residue, calcium, magnesium, ammoniacal nitrogen, nitrates and nitrites using UV VIS spectrophotometer.

For total hardness determination, the water sample was heated to about 50°C, 1 cm³ of ammonium chloride buffer solution was added to bring the pH of the solution to 10 and about 0.1 g of eriochrome black T. Samples were titrated with EDTA solution until the color changes from red to clear blue.

For the determination of the fixed residue, a volume of 50 ml measured from the filtered water to be analyzed in a volumetric flask, was placed in a porcelain capsule of known mass and evaporated in a water bath; the remaining residue was dried for two hours in an oven at 105-110°C, cooled in a desiccator and weighed; the operations were repeated until it is brought to a constant mass. It was calculated by the difference in the mass of the residue in the capsule and is related to 1 l of water.

Ca²⁺ ions have the property of forming stable complex combinations with complexon III solution (EDTA) at pH = 12-13. The determination of magnesium ions in the sample analyzed in equivalent form was carried out by calculating the difference between the total hardness and the content of Ca²⁺ ions, expressed in equivalent form.

The wells in the Șimnicu de Sus commune were numbered from 1 to 5, as follows: F1, F2, F3, F4, F5. In Figure 1, the studied wells are located, as follows:

F1- the public well is located in the suburbs of the commune, in a residential area. The fountain is in good condition, its construction being recently renovated. There are no sources in the area that could lead to water impurification, this well being one of the water sources of the locals in the area.

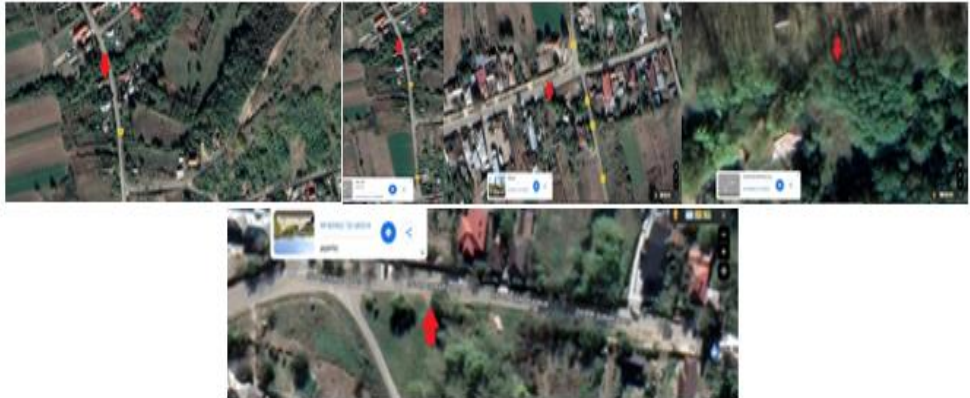


Figure 1. The location of the studied wells (google maps)

F2 – the well serves the inhabitants of the commune, it does not show a high degree of deterioration, there are no sources of pollution in the area.

F3 - the well is located in the S part of the locality and serves the inhabitants of the commune. Considering the presence of some sheepfold in the area, the quality of the water is poor, as it has not been used lately.

F4 - the well was in the center of Milești village, in a residential area near the church, being used by the locals for their own consumption.

F5 - the well is located in the N part of the locality, in the forest fund managed by the Amaradia Forestry.

RESULTS AND DISCUSSIONS

From a methodological point of view, the study of the quality of underground water in the area of the Șimnicu de Sus commune involved the analysis of the data obtained from 5 wells (F1, F2, F3, F4, F5), from March to May 2023 and the temporary identification of the exceeded established limits by the legislation in force regarding the quality of drinking water for the following indicators: pH, electrical conductivity, total water hardness, fixed residue, ammonium (NH_4), calcium, magnesium, nitrates and nitrites. The maximum allowed values for the water quality parameters are expressed according to the STAS in force as allowed values and exceptional values. The values obtained from the analysis of the water from the studied wells are compared with the values from the legislation in force.

Romanian regulations indicate a pH of drinking water between 6.5-8.5 pH units, although ideally it would be a value as close as possible to that of blood (7.35). If the pH drops below 5.6 units, the water becomes too acidic and can lead to irreversible changes in the epithelia, and if it is higher than 11, the water is much too alkaline and affects the eyes, the skin, irritating them. The ideal and recommended pH for health is 7, a completely neutral value.

The pH recorded values between 7.47 and 7.59 pH units for all 5 sampling points, values that fall within the limits allowed by the legislation in force, not exceeding the exceptionally allowed value of 8.5 pH units (Figure 2).

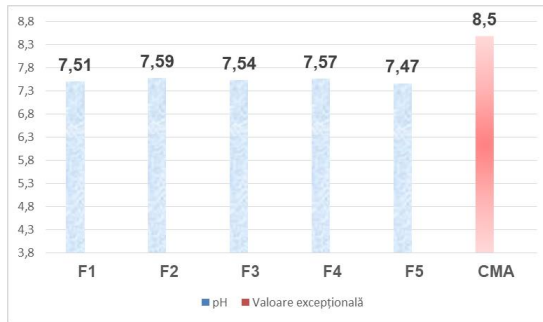


Figure 2. The pH value of water samples

Water in general, regardless of the source, contains besides molecules of H₂O (pure water) and a lot of other substances. The conductivity of water gives us information about its chemical composition and represents its charge in salts. The electrical conductivity of water represents the property of that solution to conduct the electric current, depending on the amount of ions present in the water. Water conductivity is an easy test to perform, which informs on water quality; this test is used as a way to monitor changes in the ion composition of a lake or spring using a sensor. The conductivity values will change when salts, acids or soluble gases are introduced into the water, also when the sensor is introduced into hard water.

Therefore, as the concentration of ions increases, the conductivity increases. Since conductivity values are generally very small, results are displayed using a sub-unit of the siemens, microsiemes/cm.

The standard value of drinking water conductivity is between the following accepted values, from 1000 to 3000 $\mu\text{S}/\text{cm}$ according to STAS 1342/91. Also, some studies state that if there are fluctuations in the conductivity value, the water could be contaminated.

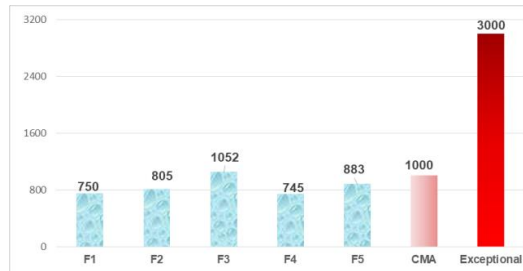


Figure 3. The conductivity value ($\mu\text{S}/\text{cm}$) of water samples

In all 5 sampling points in the Șimnicu de Sus area, the conductivity recorded values between 745 and 1052 $\mu\text{S}/\text{cm}$. From the 5 analyzed points, in 4 points, namely F1, F2, F4, F5, conductivity values were recorded lower than those stipulated in STAS 1342/91, which stipulates that the maximum allowed limit of electrical conductivity is 1000 $\mu\text{S}/\text{cm}$ and exceptionally 3000 $\mu\text{S}/\text{cm}$.

From figure 4 it can be observed that the total hardness values analyzed for the 5 water samples were between 23.1 and 37.18 German degrees, for well F3 the value of 37.18 German degrees was recorded and the maximum limit stipulated by STAS 1342/91, was exceeded, which is 30 German degrees, thus indicating a higher content of calcium and magnesium.

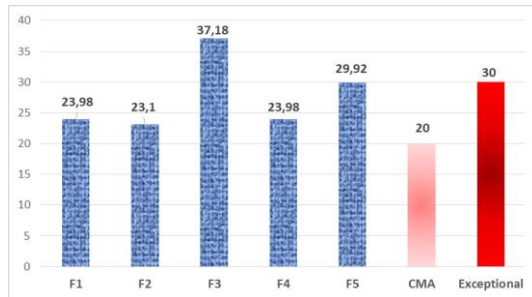


Figure 4. Total hardness (German degrees) of water samples

The fixed residue content analyzed in all 5 samples had values between 372 and 526 mg/dm³, all these values falling within STAS 1342/91 (Figure 5).

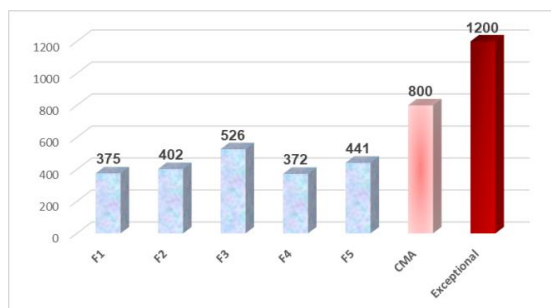


Figure 5. Fixed residue content (mg/dm³) of water samples

The ammonia nitrogen content recorded values between 0.082 mg/dm³ (F5) and 0.930 mg/dm³ (F4). If we refer to the minimum limit provided by STAS 1342/91, in all 5 wells from which the water samples were taken, the allowed limit is exceeded, which is established as having a value of 0 mg/dm³ and exceptionally 0.5 mg/dm³. This is explained by the fact that, starting from spring, the activity of microorganisms in the soil is triggered and chemical fertilizers are used that can leach onto the soil profile and thus reach the groundwater table, which it pollutes. If we refer to the maximum value allowed by STAS, then the samples collected from wells F1, F2, F4 are below the allowed limit (0.5 mg/dm³) in terms of ammoniacal nitrogen content and only the samples collected from wells F3 and F5 register values of 0.756 mg/dm³ and 0.930 mg/dm³ that exceed the exceptional limit provided by the legislation.

The calcium content determined in the 5 samples recorded values between 83.2 (F2) and 102.4 mg/dm³ (F3). Taking into account that the legal limit for calcium is 100 mg/dm³, it is observed that the values obtained for wells F1, F2, F4 and F5 are below the allowed limit, and only for well F3, this limit is exceeded (figure 7).

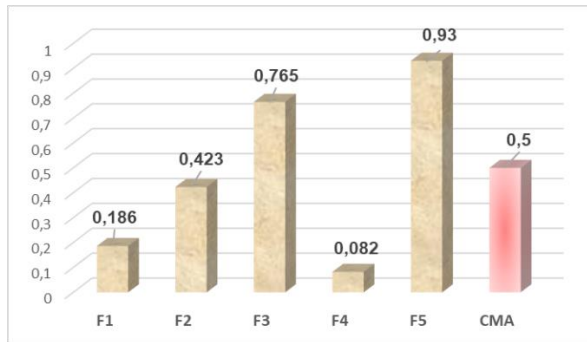


Figure 6. Ammonia nitrogen concentration (mg/dm³) of water samples

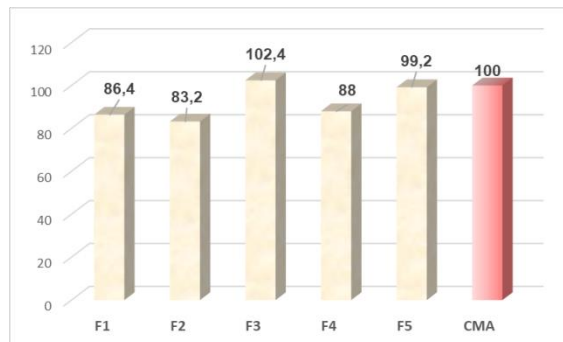


Figure 7. The calcium concentration (mg/dm³) of t water samples

Calcium is found in water in the form of bicarbonates, sulfates and chlorides. Being insoluble salts, in high concentrations they can harm the human body. In excess and together with magnesium, it creates the effect of hard water and produces malfunctions of devices and installations that use water as a technological agent in the domestic and industrial fields. In high concentrations it also damages the human body.

Regarding the magnesium concentration, the same trend of exceeding the maximum allowed limit is observed in sample F3 (101.65 mg/dm³), the rest of the analyzed samples registering values below the limit (Figure 8).

This tendency to exceed the maximum allowed limit for the F3 sample for both calcium and magnesium correlates with the total hardness, which for the F3 sample also exceeded the allowed limit, having values of 37.18 German degrees. The total hardness for sample F3 being higher, automatically indicates a higher content of calcium and magnesium in that sample.

Regarding the nitrate concentration existing in the 5 wells on the territory of the Şimnicu de Sus commune, we can state that only in wells F1 and F2 where values of 23.18 mg NO₃/l and 41 mg NO₃/l were recorded, respectively, the content of nitrates are below the maximum allowed limit of 50 mg NO₃/l. The samples collected from wells F3 and F5 recorded values of 67.25 mg NO₃/l and 73.10 mg NO₃/l respectively, in the two wells the maximum permissible limit for nitrates is exceeded (Figure 9).

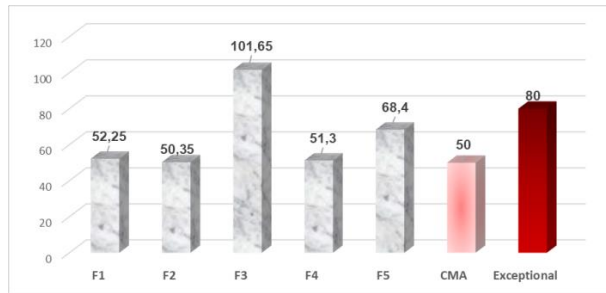


Figure 8. The magnesium concentration (mg/dm³) of water samples

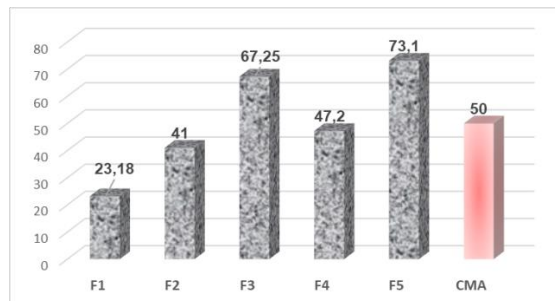


Figure 9. The nitrate concentration (mg NO₃/l) of water samples

Taking into account the results obtained, it is recommended that the water from wells F3, F4 and F5 should not to be consumed by the population of the area. Although the values obtained do not far exceed the maximum permissible limit, the cumulative effect of nitrate ingestion in the human body from water and vegetable products must also be taken into account. The World Health Organization recommends that the daily consumption of nitrates should not exceed 222 mg NO₃/day. It has been found in many cases that this dose can be exceeded very easily because if we drink 2 l of water/day as recommended, water containing 50 mg NO₃/l, we ingest 100 mg NO₃ and if we also eat 100 gr of salad containing 300 mg NO₃, we end up ingesting 400 mg NO₃ in just one day. Nitrates are not considered carcinogens, but in the gastrointestinal tract of humans and animals they are converted into nitrosamines, which are considered carcinogens.

Regarding the nitrite concentration, it can be observed that in all 5 analyzed samples, the recorded values fall below the maximum admissible limit, recording values between 0.1 and 0.5 mg/l.

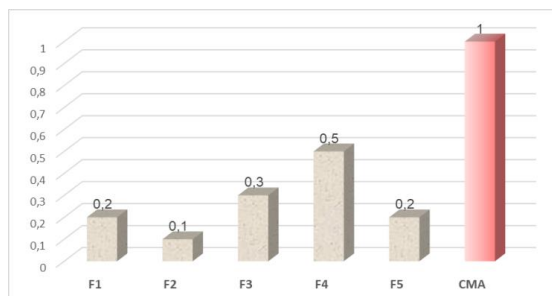


Figure 10. The nitrite concentration (mg NO₂/l) of water samples

CONCLUSIONS

The increase in anthropogenic impact due to population growth and its needs have led to numerous changes in the structure and functionality of the natural environment. Since groundwater has decisive implications in the evolution and dynamics of other elements of the natural environment, it is necessary to know and study their quality.

From the analysis of groundwater that serves as a source for public wells located in Simnicu de Sus commune, the following conclusion can be drawn:

- the pH for all 5 water samples taken recorded values that fall within the limits allowed by the legislation in force, not exceeding the exceptionally allowed value of 8.5 units;

- the conductivity of the analyzed water samples recorded values between 745 $\mu\text{S/cm}$ and 1052 $\mu\text{S/cm}$. From the 5 samples, in 4 points namely F1, F2, F4, F5, conductivity values were lower than those stipulated in Stas 1342/91, and sample 3 recorded slightly high values;

- the total hardness values analyzed for the 5 water samples were between 23.1 and 37.18 German degrees, only for well F3 the value of 37.18 was recorded, the maximum limit stipulated by STAS 1342/91 was exceeded;

- the fixed residue concentration analyzed in all 5 water samples had values between 372 and 526 mg/dm^3 , all these values falling within STAS 1342/91;

- the ammoniacal nitrogen concentration of the samples collected from wells F1, F2, F5 falls below the allowed limit (0.5 mg/dm^3) and only the samples collected from wells F3 and F4 register values of 0.756 mg/dm^3 and 0.930 mg/dm^3 that exceed the exceptional limit provided by the legislation;

- the calcium concentration determined recorded values between 83.2 (F2) and 102.4 mg/dm^3 (F3). The values obtained for wells F1, F2, F4, F5 were below the allowed limit, and for well F3 the legal limit of 100 mg/dm^3 was exceeded;

- the magnesium concentration exceeds the maximum allowed limit in sample F3 (101.65 mg/dm^3), and the rest of the analyzed samples recorded values below the limit;

- the nitrate concentration recorded values, for wells F1 and F2, of 23.18 $\text{mg NO}_3/\text{l}$, respectively 41 $\text{mg NO}_3/\text{l}$, values that fall below the maximum allowed limit of 50 $\text{mg NO}_3/\text{l}$, and for wells F3 and F5 recorded values of 67.25 $\text{mg NO}_3/\text{l}$ and, respectively, 73.10 $\text{mg NO}_3/\text{l}$, values that exceed the maximum permissible limit for nitrates;

- the nitrite concentration in all 5 analyzed water samples fell below the maximum admissible limit, being recorded values between 0.1 and 0.5 mg/l .

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