Original Article

The influence of intensive fertilization on some indicators of groundwater quality in the area of the Western Plain of Romania

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Abstract

After the change of the communist regime and the takeover of agricultural areas by private permits, they, in the context of the presence on the market of a limited range of chemical fertilizers at low prices, began their irrational application, in order to obtain large yields. Although most farmers currently apply fertilizer resources on a scientific basis, the effect of previous practices is still felt, affecting groundwater quality. This paper aims to assess the impact of chemical fertilizers on water quality indicators in a former rural area, now peri urban in the Banat Plain. 10 water sampling points were established (wells and boreholes), and the sampling was done over a period of 6 months (from November 2020 till June 2021). The parameters determined and the range of values were: pH: 6,65 ÷ 7,90; NO3- (mg·l-1): 1,23 ÷ 158,15; NO2- (mg·l-1): 0 ÷ 10,76; NH4+ (mg·l-1): 0 ÷ 5,12, EC (µS/cm): 420 ÷ 1918; PO43- (mg·l-1): 0,0107 ÷ 1,518; Cl- (mg·l-1): 9,35 ÷ 174; SO42- (mg·l-1): 18,79 ÷229,18. The interdependencies between these parameters were also studied.

Keywords: groundwater, pollution, agricultural sources.

1. INTRODUCTION

Along with large urban agglomerations and industry, agriculture, through intensive field crops and huge animal breeding complexes, represents an important source of water pollution, both surface and underground. Water pollution from agricultural sources, resulting from the loss of nutrients, amendments and irrationally applied pesticides has the effect of destroying ecosystems and the environment, and increasing the costs of obtaining drinking water, new and expensive techniques being required to obtain water suitable for human consumption [1]. In developed countries as well as developing countries, water pollution from agricultural sources has outranked that from industry and settlements. The development and intensification of cropping and livestock systems in order to satisfy the food requirements of a population in continuous expansion, puts an increasing pressure on maintaining the quality of surface and underground waters within reasonable limits for potability [2]. The main pollutants of an agricultural nature for water are: fertilizers, pesticides, metals, salts, sediments, organic carbon and drugs residues, which, through direct runoff into ditches and streams and percolation into underground waters, reach the surface through springs or channels that connects groundwater to marshes and swamps [3, 4].

Chronic water stress, as observed in many areas, is associated with both water quantity and quality, affecting every aspect of life, from the environment and ecosystems to food security and poverty. Due to its very low accessibility, water has become a rare commodity, unable to satisfy the per capita needs of urbanization and industrialization, agriculture, on top of which global warming is also superimposed [5].

Currently, Romania annually consumes approx. 3 million tons of fertilizers, being half of the consumption of fertilizers in EU countries, with an annual increase of 2-3% [6]. The increase in the price of chemical fertilizers, Romania's accession to the European Union and the implementation of European legislation has determined in recent years the application of fertilizer resources on scientific bases, in doses carefully calculated according to the supply of the soil, the needs of the cultivated plant, precipitation and temperature, so that they fulfill the role as much as possible, avoiding their penetration into the water. In the Western Plain of Romania, where the studied area is located, agriculture occupies an important part in the region's economy. The studied area (with an area of 97 sqkm), is currently part of the peri-urban area of the city of Timișoara – the largest city in the Western Plain. 20 years ago, this region was surrounded by agricultural lands, on which an intensively chemicalized agriculture was practiced, a fact that left its mark on the quality of the underground water.

2. Materials and methods:

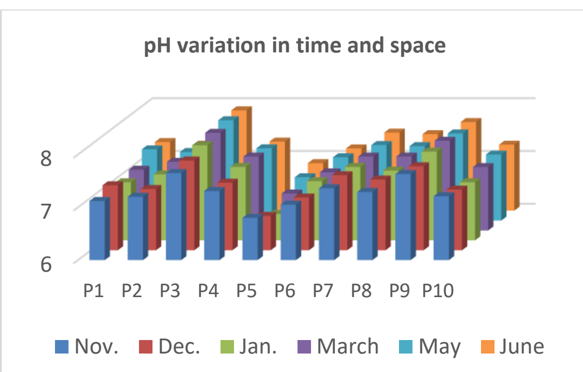
In the studied area, Sânandrei commune (45°51'12.2"N 21°10'05.2"E), 10 groundwater collection points (wells and boreholes) were established (P1, P2, P3 - public boreholes with a depth of 75-100 m and P4 – P10 - old private shallow wells, with a depth of 5 – 15 m), intended for drinking water consumption. Harvesting was carried out monthly, over a period of 6 months (November 2020 – June 2021). The samples were collected in plastic containers, pre-washed with non-ionic detergents and rinsed with deionized water. Before the samples were collected, the containers were rinsed 2 times with target groundwater. After harvesting, the samples were refrigerated and transported to the Laboratory of physical-chemical analyzes for soil-water-fertilizers, within the University of Life Sciences "King Mihai I" from Timișoara. The following quality indicators of groundwater used for drinking purposes were determined: pH, NO3-, NO2-, NH4+, PO43-, EC (electrical conductivity), Cl-, and SO42-.

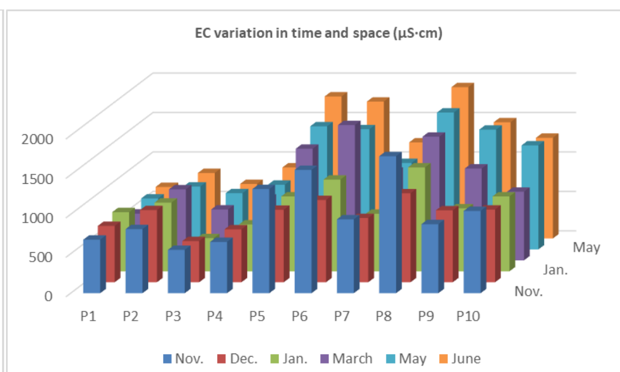
The pH was determined by the conductometric method, using a Mettler Toledo pH meter. The content of nitrates (after removal of nitrites and reduction of nitrates to nitrites) and nitrites was determined by the UV-VIS spectrometry method at the wavelength λ = 520 nm [7]. The ammonium content was determined by the Nessler method after pretreatment with EDTA to remove turbidity-causing substances, at the wavelength λ = 425 nm [8], and the phosphate content by the method of ammonium molybdate and stannous chloride, at the wavelength λ = 715 nm. Chlorine and sulfate content was determined by the volumetric method, titration with AgNO3 in the first case, respectively BaCl2 in the case of sulfate. EC was determined by the conductometric method, using a Mettler Toledo conductometer.

3. Results and discussions

The obtained values are presented in Table 1, being expressed as mean ± SD (standard deviation).

The variation of quality indicators monitored over time and in the studied area is represented in figure 1.





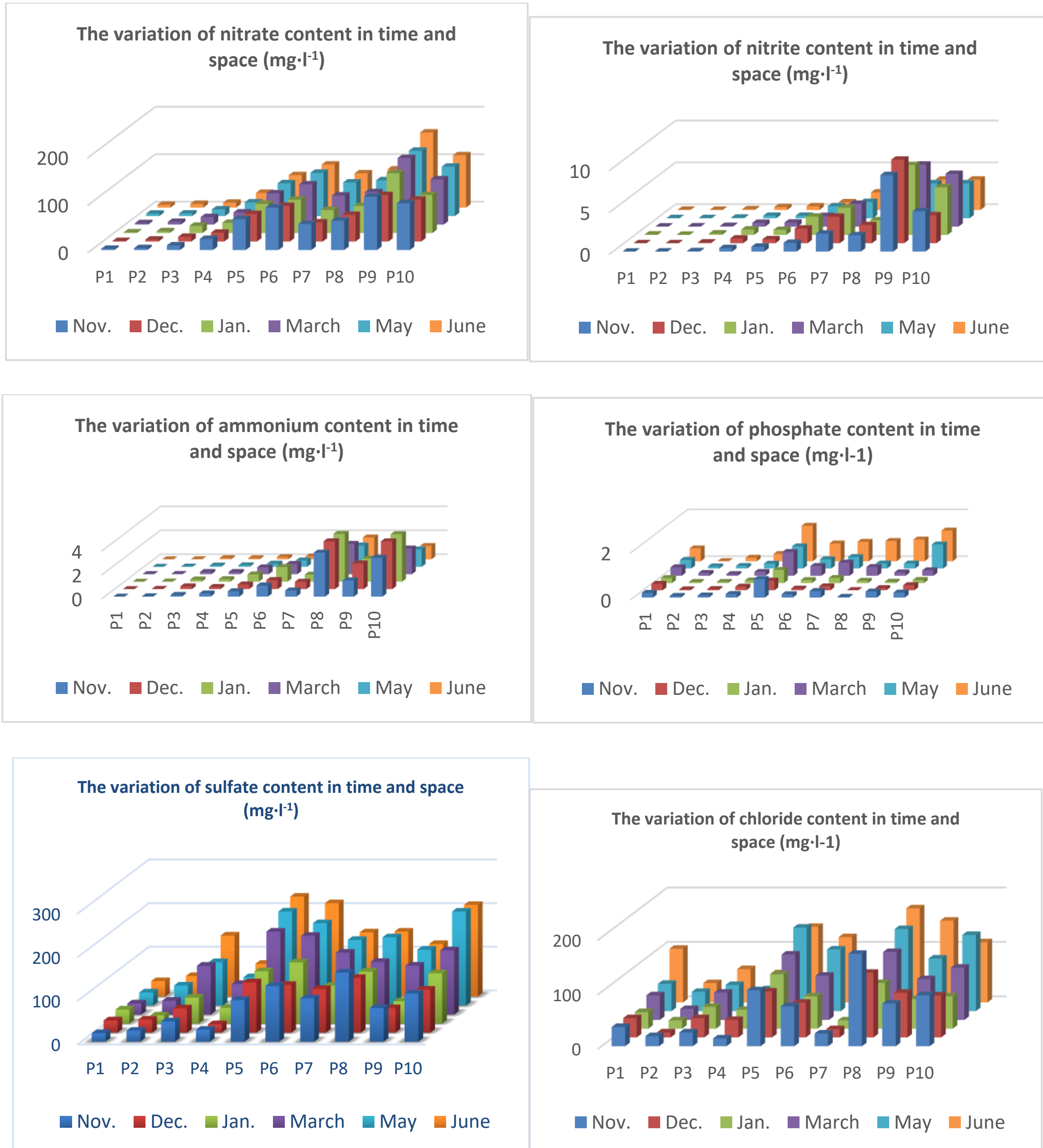


Fig.1. Variation of groundwater quality indicators, in the period Nov. 2020 – June 2021, in West Plain, Sânandrei commune

3.1. pH

The pH values of the underground water samples during the monitored period were ranged between: 6.5 ÷ 7.9, values that fit the collected samples into the category of water that can be used for drinking purposes. The lowest value, at the lower limit of the allowed range for drinking water (6.5 ÷ 9.5), according to EU directive 2020/2184 [9] was determined in January - 2021, in the P5 collection site. Bibliographic data indicate that long-term use of both nitrogen and phosphorus fertilization leads to slight acidification of groundwater, the more pronounced the deeper the aquifer is.

3.2. Nitrates and nitrites

Nitrates are present in waters naturally, being part of the nitrogen cycle. Nitrates can reach both surface and deep waters as a result of anthropogenic activities, such as excessive fertilization, both mineral and organic [10, 11]. The nitrate content of water sources has an increasing trend in the future due to population growth, the amount of nitrogen fertilizers used and the density of livestock [12]. On the other hand, by altering the hydrological cycle, climate change will affect the nitrogen content of surface and groundwater, because the amount, intensity and timing of precipitation affect the level of nitrates in water [13]. Under oxidizing conditions, in groundwater, nitrates represent the most stable form of nitrogen, while nitrites are a labile form, originating from the incomplete reduction of nitrates in anoxic aquifers [14].

The nitrate content in the groundwater samples, collected in the interval Nov. 2020 – Jun. 2021, is located in the interval 1.23 ÷ 158.15 mg NO3-·l-1. Considering that the maximum limit allowed by the WHO for the content of nitrates in water used for drinking purposes is 50 mg mg NO3-·l-1, analyzing the data presented in fig.1 it is observed that more than 50% of the samples exceed the maximum allowed limit. The highest values, in the range of 80.18 ÷ 125.8 mg NO3-·l-1, were determined at collection points P9 and P10. Also, the highest values were determined in Nov. 2020, respectively June 2021, values justified on the one hand by the low rainfall during that period, which determined the concentration of nitrates in underground waters. Low values of the nitrate content were determined in the collection points P1-P4, in the range of 1.23 ÷ 31.04 mg NO3-·l-1, values that allow the use of these waters for drinking purposes.

The nitrite content determined in the groundwater samples is located in the range 0 ÷ 10,76 mg NO2-·l-1. The highest values, of approx. 20 times higher than the maximum allowed limit for water used for drinking purposes (according to WHO) were determined in P9, in the months of November 2020 (9.15 mg NO2-·l-1) and December 2020 (10,76 mg NO2-·l-1). The only collection points that fall within the standards set worldwide for drinking water (0.5 mg NO2-·l-1) are P1, P2 and P3, boreholes with deep groundwater. In general, the nitrate content had the highest values in the months with low temperature (Nov., Dec., Jan.) (Fig.1)

3.3. Ammonium

Ammonium is considered one of the most alarming pollutants of the aquatic environment not only because of its toxic nature, but also because of its ubiquity. Generally in groundwater, the ammonium content is less than 0,2 mg NH4+·l-1 [15, 16].

The ammonium content determined in the groundwater samples is located in the range 0 ÷ 5.12 mg NH4+·l-1, the highest values being determined at the collection point P8, in the months of December 2020 (5.12 mg NH4+·l-1) and January 2021 (4.96 mg NH4+·l-1). Approximately 50% of the analyzed samples exceed the maximum allowed limit of 0. mg NH4+·l-1 for ammonium in drinking water. The lowest values (0 ÷ 0.26) were determined in collection points P1-P4.

3.4. Electrical conductivity

According to WHO standards, the electrical conductivity values recommended for water used for drinking purposes must not exceed 400µS·cm-1. The values determined for the collected samples were located in the range 420 ÷ 1918 µS·cm-1. The highest values were determined in collection points P4-P10, values that may be due to the high content of dissolved positive and negative ions, organic pollutants as well as clay particles in suspension [17, 18, 19, 20, 21].

3.5. Phosphate

P compounds having much lower solubility compared to nitrogen compounds, so they tend to be adsorbed by soil colloids [22]. Following the saturation of the colloidal complex, the phosphates are released into the soil solution and end up being transported to the groundwater [23]. Even if the amount of P fertilizers applied is reduced, soil-adsorbed P—a legacy of past agricultural practices—can be mobilized, thus representing a major source of groundwater pollution [24]. Overall, 40% of the phosphorus discharged into freshwater ecosystems is attributed to agriculture.

The phosphate content determined in the analyzed groundwater samples is in the range of 0.0107 ÷ 1.518 mg PO43-·l-1. 3 of the analyzed samples exceed the maximum limit allowed worldwide for the phosphate content in drinking water (1 mg PO43-·l-1, according to 39), namely in June P5 (1.518 mg PO43-·l-1) and P10 (1.314 mg PO43-·l-1), respectively in May P10 (1.031 mg PO43-·l-1). Considering the low level of phosphates determined in the other months in all collection points, these high values are due to accidental pollution. Overall, the highest values of the phosphate content in the underground water are recorded in the month of June. (Fig.1).

3.6. Sulphate

In groundwater, S is found predominantly in the form of sulfates, which are stable and highly soluble and also highly mobile in the aquifer system [25]. Because of this, in general the sulfate content is high, having both natural and anthropogenic causes. The last category includes power plants, coal mining, metallurgical industry and agriculture [26].

The maximum allowable limit for the content of sulfates in water used for drinking purposes was established by the WHO at 250 mg SO42-/l. The sulfate content determined was in the range of 18.79 ÷ 229.18 mg SO42-/l, below the maximum allowed limit. Higher values were determined in points P5 – P10, which represent shallow groundwater sources (Fig.1).

3.7. Chloride

A significant amount of chloride enters groundwater from anthropogenic sources, namely municipal waste, sewage, and manure from livestock farms [27]. As a rule, groundwater has a low chloride content (less than 10 mg Cl-·l-1). A high content exceeding 20-30 mg Cl-·l-1 is due to the contamination of water with animal waste, the septic system, as well as the intensive use of agricultural land (31). The values determined in the analyzed samples were located in the range of 9.35 ÷ 173 mg Cl-·l-1, values that do not exceed 250 mg Cl-·l-1 (maximum allowed limit). The highest values were obtained in samples collected from points P5-P10.

3.8. Statistics:

To study the dependence between the analyzed indicators, the Pearson correlation was performed, using SPSS.

TABLE 1: Pearson Correlation Coefficient Matrix

	pH	Nitrate	Nitrite	Ammonia	Phosphate	EC	Sulphate	Chloride
pH	1							
Nitrate	-,002	1						
Nitrite	,242	,715**	1					
Ammonia	-,029	,423**	,442**	1				
Phosphate	-,360**	,375**	-,040	-,141	1			
EC	-,283*	,627**	,076	,304*	,545**	1		
Sulphate	-,212	,626**	,151	,264*	,647**	,780**	1	
Chloride	-,220	,600**	,156	,425**	,558**	,778**	,708**	1

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

Analizising data presented in table 2, we found signifficant positive correlations at P<0,01 between nitrate – nitrite; nitrate – ammonium; nitrite – ammonium; nitrate – EC; nitrate – phosphate; sulphate – nitrate, sulphate – phosphate; chloride – nitrate, chloride – ammonium; chloride – sulphate; chloride – phosphate; chloride – EC. Signifficant negative correlation at P<0,01 was found between pH – phosphate. Signifficant pozitive correlation at P<0,05 were found between ammonium – EC and ammonium – sulphate and signifficant negative correlation at P<0,05 between pH – EC.

4. Conclusions:

In areas where intensive agriculture has been practiced, there is a degradation of the quality of underground water, often used as sources of drinking water.

Although a much more rational application of fertilizing resources, both mineral and organic and mineral, is currently being tried, the legacy of previous years still makes its presence felt. Shallow groundwater is much more affected by the presence of nitrates, nitrites, ammonium, phosphates than deep ones.

The presence of significant correlations between the content of nitrates, ammonium, phosphates and chlorides supports the statement that a soil subjected to intensive agriculture ends up having a high content of chlorides, which will later be washed into the groundwater.

In the studied area, on top of the agricultural pollution, there is also a point pollution, due to the infiltration into the shallow groundwater of animal droppings from the households as well as insufficiently waterproofed septic tanks.

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