Carpathian Journal of Earth and Environmental Sciences, August 2019, Vol. 14, No. 2, p. 323 - 334; DOI:10.26471/cjees/2019/014/083

INFLUENCE OF DOMESTIC ACTIVITY ON THE QUALITY OF GROUNDWATER AND SURFACE WATER IN THE RURAL BUILT-UP AREA OF THE SOUTHERN ROMANIAN DANUBE PLAIN – A CASE STUDY IN THE GLAVACIOC CATCHMENT

Radu LĂCĂTUŞU, Cristian PALTINEANU[1], Andrei VRINCEANU, & Anca Rovena LĂCĂTUŞU

National Research and Development Institute for Soil Science, Agrochemistry and Environment - ICPA Bucharest, B-dul Marasti, no. 61, 011464 Bucharest, Romania. [1]Corresponding author, email: cristian_paltineanu@yahoo.com

Abstract: This paper characterizes the present-day quality of groundwater from the Glavacioc catchment and tests the existence of significant differences between the chemical components of the groundwater and surface water. Water samples were collected from wells located in the built-up area of villages and from the surface water of the Glavacioc River. There was a large spatial variability among the chemical components from both groundwater and surface water. The means of some pollutants (N-NO_3) exceeded the permissible values established by the law; however, other ions like SO_4^{-2}, Cl^-, Na^+ and electrical conductivity also exceeded the limits as individual values, but only in some wells. The existence of some harmful anions to human health, like N-NO_3, from the wells situated within the built-up area of villages does not necessarily demonstrate their leaching from the arable land toward the groundwater, but rather deficiencies of hydrological isolation of the nitrate sources from human households.

Keywords: nitrate pollution, anion & cation water content, electrical conductivity, heavy-clay soils, household activities

1. INTRODUCTION

Ground water and surface water have long been used for various purposes, including drinking, irrigation and industry consume. Water quality and quantity are the main criteria used for human and animal consume. The chemical composition of groundwater generally depends on the soil-plant-atmosphere continuum (SPAC) of the current environment at different scales, including land use type (forests, orchards, vineyards, pastures, arable land and human settlements), natural properties of the environment (relief, soils, geological deposits) and human activities.

Precipitation water flows through the soil and the geological deposits below, and as affect the chemical composition of ground water and surface water is substantially influenced by the water contact with the soil and rocks. Studying the interaction between the irrigation water and the environment, Grumeza et al., (1990) published results on the dynamics of water table and chemistry in irrigation systems from samples taken from both special hydro-geological wells in the agricultural fields and common wells from the built-up area of settlements. In the catchments of the southern part of the Danube Plain, specifically in the interfluves between the Olt and Arges Rivers to which the Glavacioc Catchment belongs, these authors emphasized the “high level periods” of water table, specifically after the establishment of the irrigation systems, from which there was important leaching and sometimes overdoses of water application. Later on there were studies in the region recommending rational irrigation application to prevent deterioration of soil physical and chemical properties (Paltineanu et al., 2000). The oscillations of the water table were also influenced by the rainy or droughty character of the years.

The oil industry is well developed in the region, and the old technology applied for decades might have influenced the chemical composition of the water, mainly by injection of various fluids in the groundwater. Lăcătuşu et al., (1994), Damian et al., (2013), Lăcătuşu (2017) and Nicula et al., (2017) investigated soils and waters in various locations with regard to pollution with many ions. Pollution of water with various substances does not only occur with sodium and nitrate, but also with heavy metals (Zn, Pb, Cu, etc.), specifically in areas with mining industry in this country, as reported for health problems by Lăcătuşu et al., (1993, 1996), and recently by Ispas et al., (2018).

Agriculture uses chemicals, mainly based on nitrogen and other macro-elements, in order to increase yield. If not rationally applied, combined with overdoses of irrigation application, some chemical components might have also been leached to the groundwater and surface water. Some studies (Dumitru et al., 2009; Dumitru et al., 2013) reveal that the Maximum Contaminant Level (MCL) of nitrate as nitrogen (NO_3-N) of 10 mg/L was exceeded in the groundwater of some settlements of the Timis county; other authors also reported NO_3 values exceeding 100 mg/l in the built-up area of the Dolj county, and even outside of built-up areas (Mocanu, 2005). Dumitru et al., (2013) noted that the highest nitrate content in groundwater was found in the wells from the sandy soils (psamosols), followed by chernisols and luvisols, according to soil permeability; they also presented small-scale maps at the country level showing punctual or surface sources where the nitrate concentration exceeded MCL.

However, Dumitru et al. 2009 and Gherghina et al. 2010 reported that the nitrate concentration in the wells located on arable soils or vineyard soils is low. Nevertheless, there is no actual data on the chemical composition of the groundwater and surface water within the Glavacioc catchment, and this situation is frequently met across the country.

Recently, Canoğlu et al. (2019) used specialized models to characterize soil–aquifer interactions in the vadose zone.

The purpose of this paper is to characterize the present-day chemical composition of groundwater from the Glavacioc catchment and to test the existence of significant differences between the chemical components of the groundwater and surface water from this catchment, as well as to emphasize the causes of these differences.

2. MATERIAL AND METHODS

Glavacioc catchment is part of Arges River catchment, located in the central part of the Danube Plain and has a general north-west to south-east orientation.

Water samples were collected from wells located in the built-up area of villages within the Glavacioc catchment and nearby, and in some points also from the surface water of the Glavacioc River. These water sampling points cover the catchment area (Fig. 1). Location of the wells and places from where water samples were collected is given in Table 1, along with water table depth. Identification of these spots was done using the 1: 25000 topographic map and the GPS system combined.

The analyses of water samples were carried out according to the methodology published by Lăcătuşu et al., (2017) using the following methods: pH, anions: CO_3^{-2}, HCO_3^-, SO_4^{-2}, Cl^-, NO_3^-, cations of Ca^{+2}, Mg^{+2}, Na^+, K^+, total salts content, electrical conductivity; other current analyses were also performed.

The water table and the ground altitude are essential data for finding the direction of flow. That is why we have compared the water table from the moment of determination – spring and summer 2018 - with the depth depicted on The Hydrogeological Map of the Danube Plain, scale 1: 100 000 (**Harta hidrogeologică a României, 1970-1974), issued in years 1970s by the Geological Institute of Romania, also shown in Table 1. It has been found thus that the water table values from the two occasions are not substantially different, even if the comparison is not for the same wells and the old data have been obtained by interpolation of the water table isolines. This finding shows that the investigated catchment is relatively stable from the view point of water table.

The water properties data were processed with SPSS14 software program for analysis of variance between groundwater and surface water properties and Microsoft Excel for graphs and other statistical calculations. Because only two situations have been used for comparison, the differences between their means were tested for significance by using the *95% Confidence Interval for Mean* computed with the SPSS14 software program. The means of the treatments followed by different letters are significant for the probability $p \leq 0.05$. The symbol * was used for significant differences ($p \leq 0.05$) in the case of the correlation coefficient R; where differences are distinctly or highly significant ($p \leq 0.01$ or $p \leq 0.001$) the symbols are the well-known ones: ** and ***, respectively.

Soil data were also collected from profiles and analyzed in the lab using the methods described by Lăcătuşu et al., (2017) and existing soil maps were analyzed.

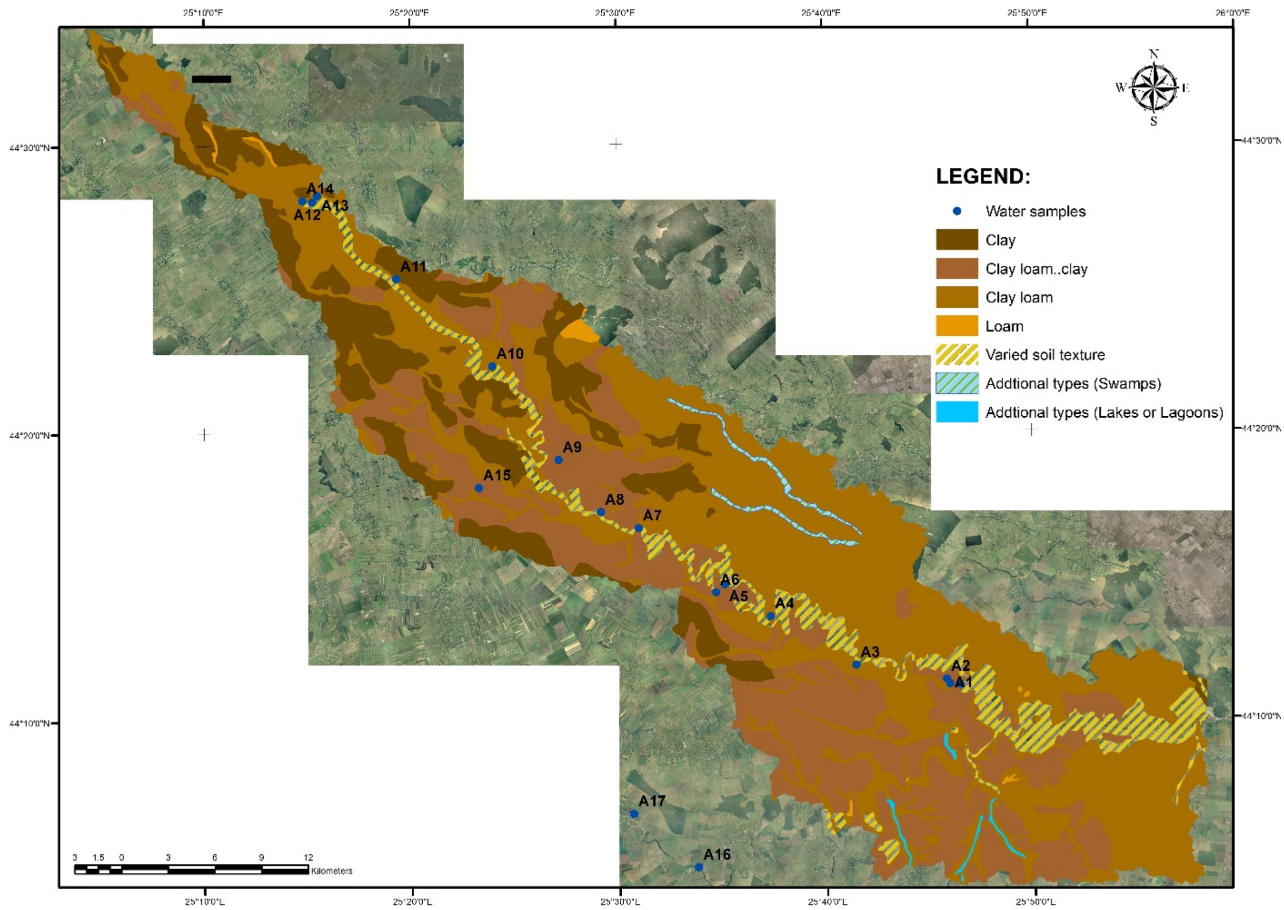


Figure 1. The topsoil texture of the Glavacioc River catchment and the water sampling points across the territory

Table 1. Geographical coordinates and altitude of the points of water sampling in the Glavacioc catchment and nearby

Symbol	Commune	Geographical coordinates		Topographic map 1:25 000	Water table measured (m)	Water table* estimate 1970 (m)
		N Latitude	E Longitude	Altitude (m)		
A1	Copaciu	44.18702	25.76461	66.5	6.5	above 5
A2	Copaciu	44.18987	25.76201	62.5	0.0 river	
A3	Letca Veche	44.19829	25.68928	92.5	21.6	above 15
A4	Merenii de Sus	44.22681	25.62061	85.5	5.2	Cca. 5
A5	Crevenicu	44.24558	25.58361	89	3.8	Cca. 5
A6	Crevenicu	44.24085	25.57686	101	30.0	above 15
A7	Videle	44.27827	25.51484	96	4.7	Cca. 5
A8	Blejești	44.28774	25.48455	98	2.0	below 5
A9	Blejești	44.31802	25.45061	113	8.2	8-9
A9	Blejești				Supply network	
A10	Puranii de Sus	44.37238	25.39761	126	11.7	10 - 12
A11	Cătunu	44.42317	25.32033	130	2.45	below 5
A12	Glavacioc	44.46777	25.25257	143	1.4	below 5
A13	Glavacioc	44.47150	25.25656	145	0.0 spring	
A14	Glavacioc	44.46840	25.24459	144	0.0 river	
A15	Cosmești	44.30198	25.38644	115.5	6.2	5 - 10
A16	Drăgănești-V.	44.08153	25.56170	71	0.0 river	
A17	Comoara	44.11271	25.50987	86	7.0	Cca. 10
A18	Copaciu	44.18671	25.77287	60.5	0.0 river	

*Depth established by interpolation of the water table isolines, Hydrogeological Map of Romania, scale 1: 100 000.

3. RESULTS

3.1. The environmental conditions in the Glavacioc catchment

The catchment altitude varies from 205 m in the upper sector to 45-50 m in the lower sector, showing a flat aspect and a low slope. The land of the Glavacioc catchment is generally used for agriculture, and the arable land use is prevalent with about 79% of the territory, followed by forests (10%), pastures (4.5%), orchards and vineyards (0.5%). The built-up area is 5.3% of the catchment. Other economic activity is the oil industry with many oil-wells spread over the entire area.

The flora is specific to forested land, with prevalent quercineae and associated herbaceous vegetation. The root system of forest trees, fruit trees (Paltineanu et al., 2016a and 2016b) and agricultural crops explores the soil and creates important channels and macropores facilitating the flow of water and solutes toward groundwater. The crop structure of the arable land consists of dominant winter cereals (wheat and barley) covering about 51.0% of the catchment area, rapeseed (20.2%), sun-flower (8.8%), peas (6.7%), chickpeas (6.4%), etc.

The climate of the catchment is temperate-continental, a Dfb category according to Köppen-Geiger climate classification (Geiger, 1961); the mean annual air temperature is 10.7°C and precipitation is 540 mm, while the UNEP* aridity index is 0.7, and the Penman-Monteith reference evapotranspiration (ETo) is 770 mm (Paltineanu et al., 2007). The trend of climate in the region has shown an increasing trend in annual temperature, ETo and crop ET (Paltineanu et al., 2011, 2012).

The parental rocks that lie beneath the soils are represented by loess, loam and especially clay deposits lying on recent geological rocks like Holocene and Pleistocene alluvial deposits of gravel and sand that frequently are aquifers.

The Glavacioc catchment soils were mainly formed on medium-fine or fine-textured geological deposits. Preluvosols cover more than 38% of the territory, and together with luvosols (more than 18%), vertosols, pelosols (more than 11%) and argic-chernic phaeozems (about 6%) combined they occupy over 80% of the catchment area. The soils' types are after Florea & Munteanu (2012).

The organic carbon content generally varies from 3.5% in the forest topsoil and 2.5% in the arable topsoil (Am horizon) to about 1% deeper in the subsoil (Bt horizon), while the mean pH values range between cca. 5.1 in topsoil and 7.4 units in subsoil. The soil content in nutrients, i.e. total nitrogen (Nt), nitrate N, ammonium N, the mobile K (K-AL) and P (P-AL), has the following values: 0.38% and 0.22% for Nt in the Am horizon in the forest and arable soils, respectively, decreasing to less than 1% deeper in the subsoil; 53 mg/kg and 44 mg/kg P-AL in Am in the two land uses, and dropping to about 5-10 mg/kg in Bt; 260-270 mg/kg K-AL in Am and 100-150 mg/kg in Bt; 140-160 mg/kg–NO_3-N in the forest topsoil versus 20 mg/kg in the arable topsoil, decreasing to 20-30 mg/kg in Bt horizon; 13-14 mg/kg NH_4-N in the Am horizon, both land uses, and 2 to 6 mg/kg in the subsoil.

In the upper soil horizon (Romanian Soil Map, scale 1: 200 000, ICPA Archive) about 49% of the catchment area present clayey-loam texture, 29% clayey-loamy-clay texture and 14%, clay texture; basically, more than 90% of the catchment area is covered by soils possessing moderate-fine texture. Over the soil profile, the clay percentage usually increases just beneath topsoil, so that in the Bt horizon the clay percentage is even higher. The topsoils' texture map is shown in Fig. 1. The texture determines many other soil properties, like the saturated hydraulic conductivity (Ksat), which shows a high spatial variability in the catchment; thus, Ksat ranges from about 20-30 mm/h in the topsoil of various land uses (forests, orchards, arable lands etc.) to less than 0.3 mm/h deeper in the subsoil of either land use (Paltineanu et al., 2019). The minimum Ksat values from the Bt horizon determine the low water and solute movement in the whole soil profile, mainly from surface toward groundwater (Paltineanu et al., 2000).

Bulk density (BD) usually ranges from about 1.1 kg/dm^3 in topsoil to a maximum of 1.6 kg/dm^3 deeper in Bt horizons, The prevalent (70% of the area) land slope of the catchment is between 0 and 0.02 m/m, followed by 0.02 - 0.05 m/m (22%) and by 0.05 – 0.08 m/m (5%). Higher slopes (above 0.15 m/m) prone to runoff and erosion are only found near valleys, occupying small areas.

Applied fertilizers on agricultural (mainly arable, then orchards, vineyards and pastures) lands are potential sources of chemical substances that might reach groundwater flowing generally to the Glavacioc River, with which interacts closely. The specialized research institution involved in the region is the Agricultural Research Station Teleorman from Draganesti-Vlasca, county Teleorman, Romania. This unit applies less than 500 kg/ha as mineral fertilizers (20:20:0 NPK complex fertilizers), Calcium ammonium nitrate, urea, ammonium nitrate and phosphate, in total as gross weight. The applied nutrients are assumed as potential sources of environmental pollution.

Water table ranges from near soil surface in the flood plains close to River Glavacioc to more than 20 m in the higher ground in the interfluves. Deep water table values are prevalent in the catchment.

3.2 Water pH

Across the Glavacioc catchment the surface water presents higher pH values, being slightly alkaline, versus the groundwater that is neutral, Fig. 2. The differences between these two water categories are significant. The water from the supply network is also neutral. The pH range was relatively narrow for both water types, namely between 0.5 and 1 unit around their means.

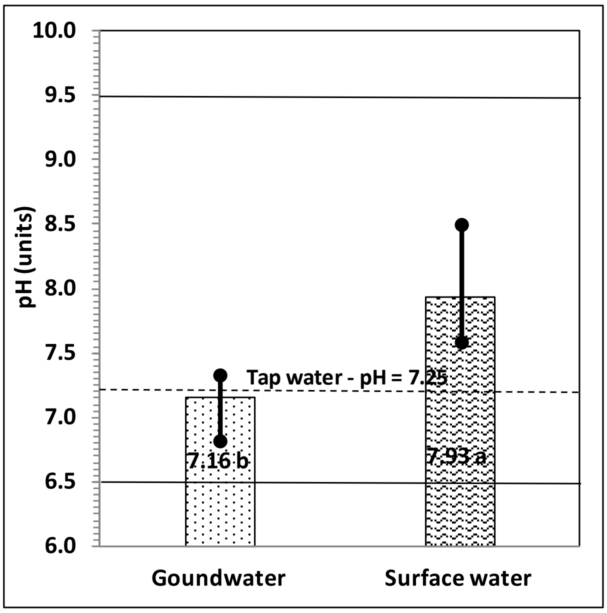


Figure 2. pH of the water body types (groundwater and surface water) investigated from the Glavacioc catchment; note here and in the following graphs that the vertical bars show the minimum and maximum values, respectively, whereas the horizontal continuous lines are the minimum and maximum permissible legal limits, respectively ***; the tap water is from the local water supply network, and the groundwater refers to the unconfined (phreatic) aquifer

3.3 Water content in HCO_3^-, SO_4^{-2}, Cl^-, NO_3^- anions

Figure 3 shows the water content in HCO_3^- that is higher, but not significantly different, in the groundwater versus the surface water; this is attributed, most probably, to the different nature of the environment through which the precipitation water flows toward both water types. The tap water presents substantially lower values.

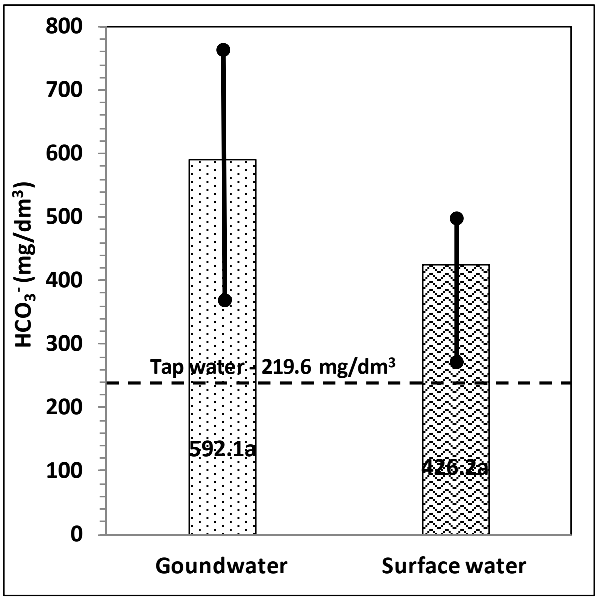


Figure 3. Water content in HCO_3^- of the water body types investigated from the Glavacioc catchment

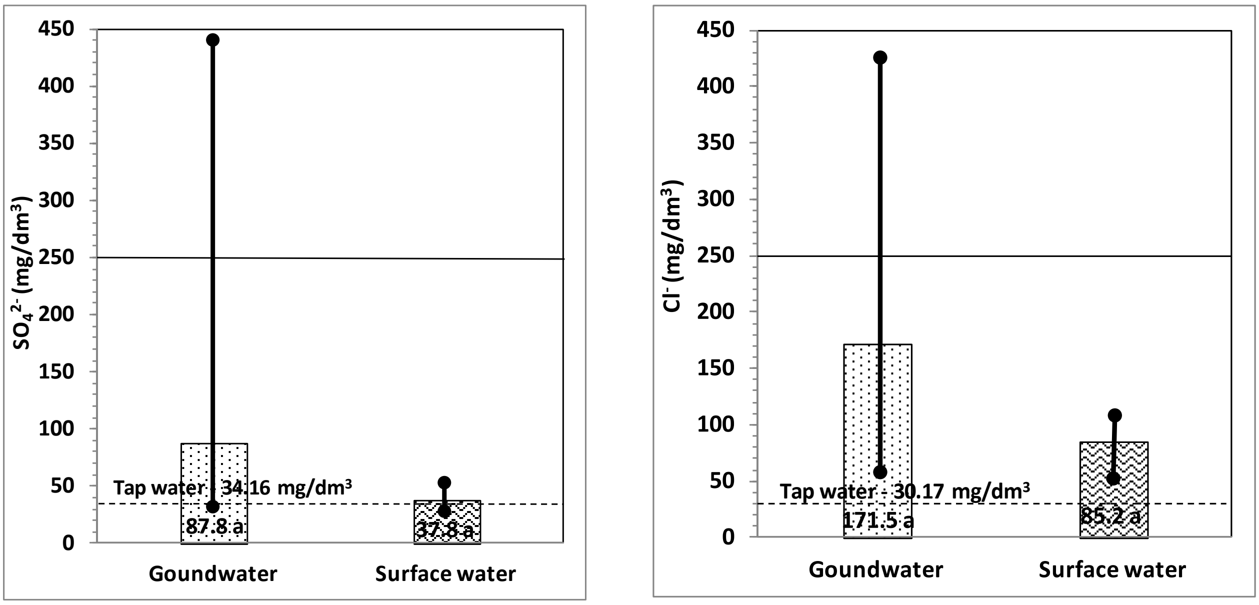
A similar situation is also found for two other anions analyzed here, SO_4^{-2} and Cl^-, with the groundwater content being higher than the surface water content; these differences are not significant either, Fig. 4a and 4b, having probably the same causes. The tap water presents a lower content in these anions.

Large amounts of nitrates have been found in the groundwater; i.e. 345 m/dm^3 (Fig. 5a), exceeding by about seven times the maximum contaminant level - MCL value that is 50 mg/l (***Romanian Act Legea 311/2004). Thus, for human consume the groundwater is not suitable from the view point of nitrate content.

Even the surface water from the Glavacioc River has presented a high content in NO_3^- (169 mg/dm^3) when the sampling point AS4 has been chosen downstream of a certain location where there has been a nitrate spill; however, upstream the AS4 point the nitrate content is low (Fig. 5b). In either of these two situations there are significant differences between the nitrate content from the groundwater, which is highly pollutant with this anion, versus the surface water of the River. The tap water from the water supply network presents low nitrate content (24 mg/dm^3) and does not cause problems to the inhabitants of the region.

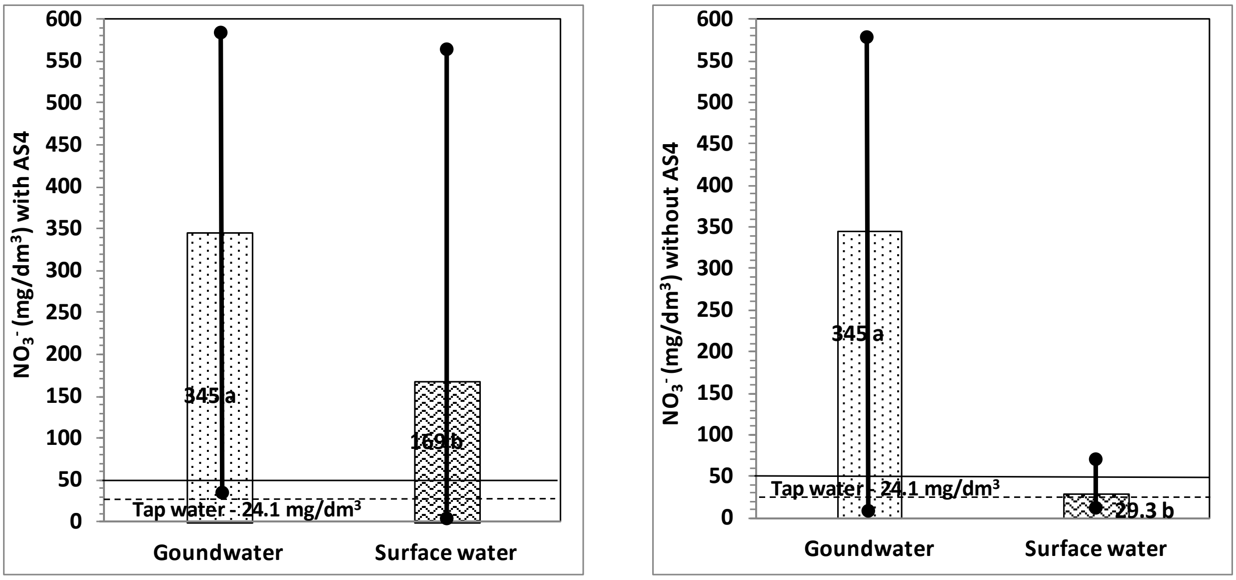
3.4. Water content in Ca^{+2}, Mg^{+2}, Na^+, K^+ cations

Groundwater contains higher amounts of Ca^{+2} and Mg^{+2} versus surface water, yet with non-significant differences between them in the case of



a) b)

Figure 4. Water content in SO_4^{-2} (a) and Cl^- (b) of the water body types investigated from the Glavacioc catchment, maximum permissible level is 250 mg/dm^3 for both aforementioned anions ***



a) b)

Figure 5. Water content in NO_3^- of the water body types investigated from the Glavacioc catchment in two situations: with all water sampling points including AS4 (a), and without AS4 (b); maximum contaminant level is 50 mg/dm^3 ***

Ca^{+2}, Fig. 6a, and significant differences in the second case, Fig. 6b. This can be explained by the enriched subsoil in these two cations and rainfall water infiltration and flow toward groundwater. Tap water presents lower Ca^{+2} and Mg^{+2} values; water hardness is higher in the case of groundwater due to the Ca^{+2} content, compared to surface water and tap water alike.

The water contents in Na^+ and K^+ are presented in Fig. 7a and 7b. The Na^+ content is higher in the groundwater versus the surface water, without significant differences between then, and the tap water shows the lowest values. The K^+ content is higher in the surface water, however with non-significant differences between the two situations. The tap water contains the lowest Na^+ and K^+ values. Because the Na^+ content mean is lower than 200 mg/dm^3, the groundwater has a normal content from this view point. Nevertheless, the permissible level of Na+ content in some wells was exceeded.

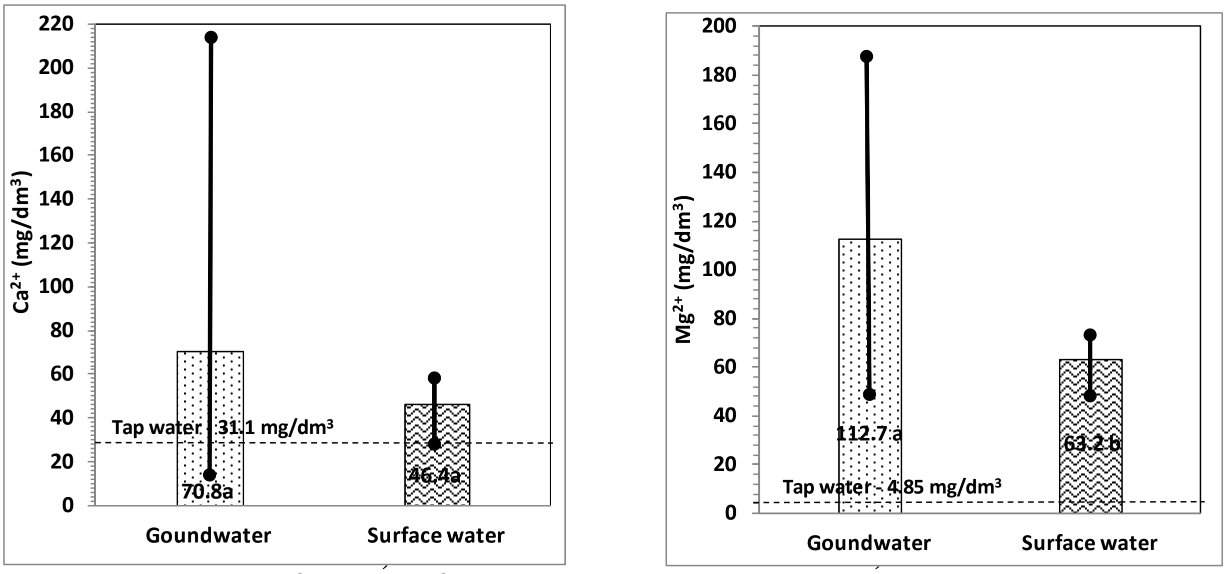
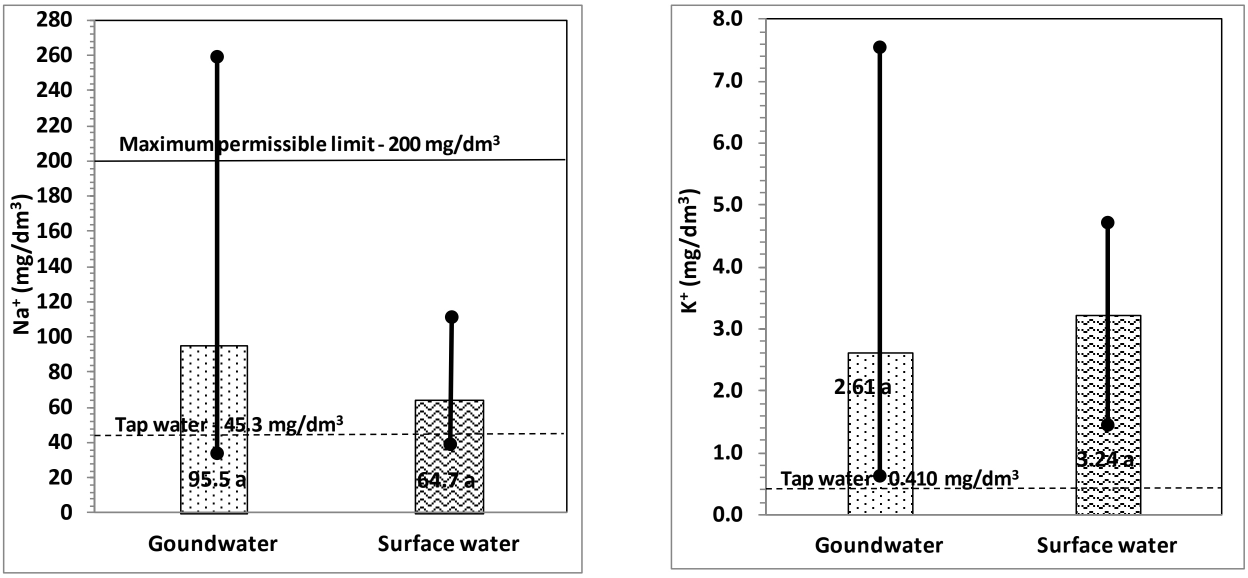


Figure 6. Water content in Ca^{+2} (a) and Mg^{+2} (b) of the water body types investigated from the Glavacioc catchment



a) b)

Figure 7. Water content in Na^{+} (a) and K^{+} (b) of the water body types investigated from the Glavacioc catchment; maximum permissible limit for Na^{+} is 200 mg/dm^3 ***

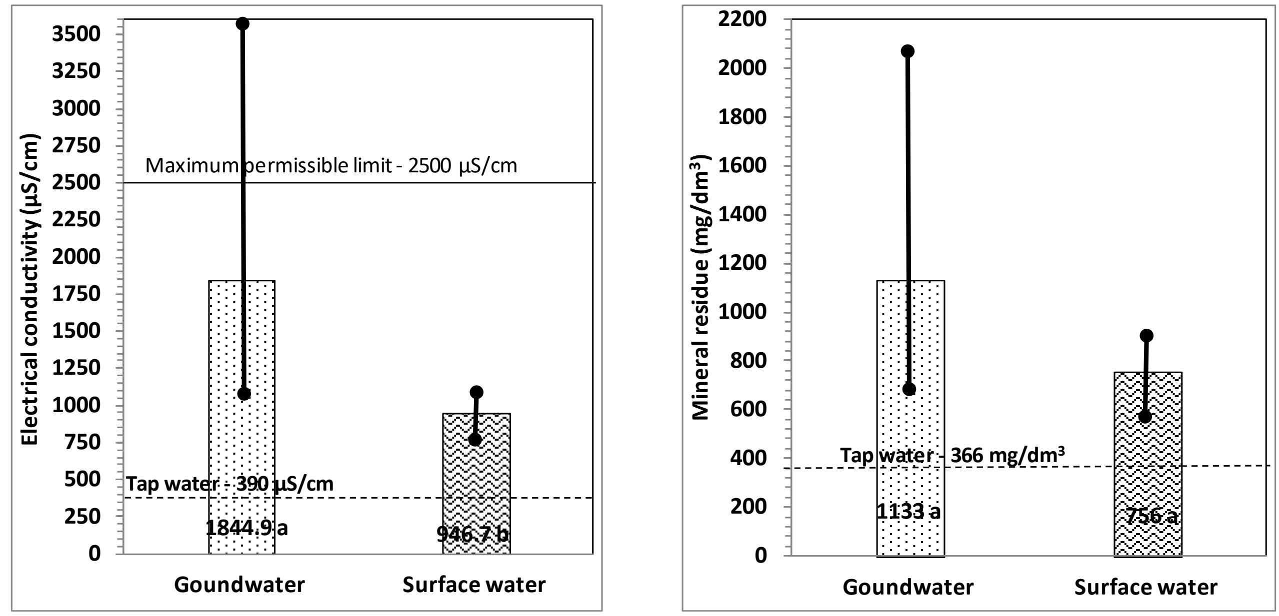
3.5. Electrical conductivity (EC) and mineral residue (MR) in water

EC is significantly higher in the groundwater versus the surface water, Fig. 8a, while MR is non-significantly higher, Fig. 8b. The lowest EC and MR values occur in the tap water.

Residual sodium carbonate (RSC) and sodium adsorption ratio (SAR) are important for water quality used in irrigation and are presented in Fig. 9a and 9b. According to RSC, the groundwater presents lower values due to the Ca^{+2} and Mg^{+2} cations` prevalence versus the HCO_3^- and CO_3^{-2} anions from the RSC formula. Because both the groundwater and surface water present RSC values that are lower than 0.5, both water types are recommendable for use in irrigation. According to SAR, both the groundwater and surface water present lower values, i.e. < 3, allowing their use in irrigation too. Unexpectedly, the tap water from the water supply system present higher RSC and SAR values.

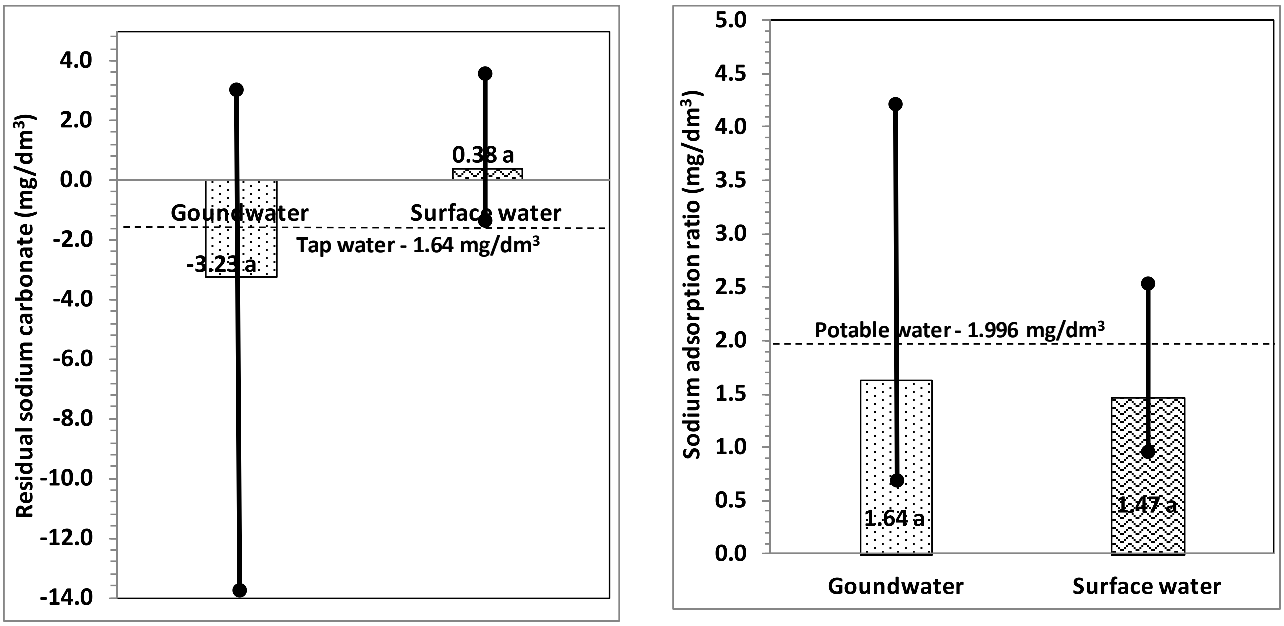
Correlations were found between water mineral residue and some water chemical components: anions (HCO_3^-, NO_3^-, Cl^-, SO_4^{-2}), cations (Na^+, Mg^{+2}, Ca^{+2}, K^+) and electrical conductivity for both water types studied.

Relationships found between water mineral residue as an independent variable and some water chemical components and electrical conductivity as dependent variables for both water types studied are depicted in Fig. 10. All the regression equations describing the correlations mentioned above are direct, and linear or curvilinear, highly significant, except the relationships between the mineral residue and Ca^{+2} cation that is distinctly significant. The highest R^2 values have been obtained for the relationships between the mineral residue and Cl^-, Mg^{+2} and HCO_3^-, while the lowest R^2 values have been found for the relationships between the mineral residue and Ca^{+2} and SO_4^{-2} ions. According to the methodology developed by Florea (1976), in all the analyzed water samples the prevalent naturally-derived anions (no nitrate) are carbonate and bicarbonate ions (73%), followed by chloride ions (18%) and sulfate ions (9%); from the cation point of view, the dominant ions are Mg^{+2} (38%), followed by Na^+ and K^+ (36%) and Ca^{+2} (26%).



a) b)

Figure 8. Electrical conductivity (a) and water mineral residue (b) of the two water body types investigated from the Glavacioc catchment; maximum EC permissible limit is 2500 µS/cm ***



a) b)

Figure 9. Residual sodium carbonate (a) and sodium adsorption ratio (b) of the two water body types investigated from the Glavacioc catchment

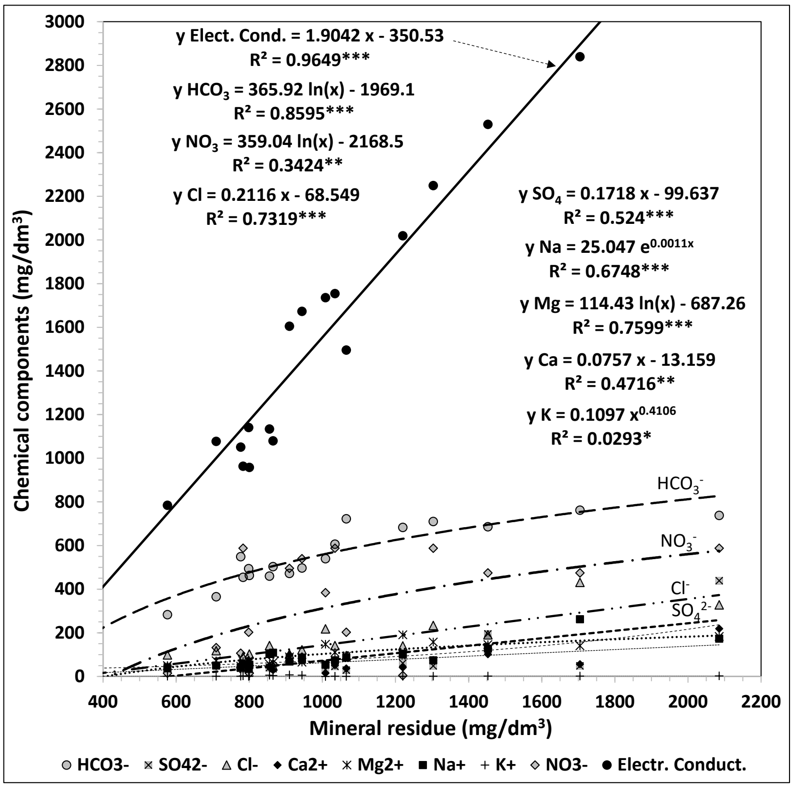


Figure 10. Relationships between water mineral residue and various water chemical components: anions (HCO_3^-, NO_3^-, Cl^-, SO_4^{-2}), cations (Na^+, Mg^{+2}, Ca^{+2}, K^+) and electrical conductivity for both water types studied; the regression equations are written up-down in the graph according to their magnitude, and *, ** and *** are significance symbols

4. DISCUSSION

The slightly alkaline chemical reaction of the groundwater and the neutral pH of the surface water are most probably caused by the mineral nature of the soils and shallow rocks from this catchment and by the nature of substances resulted from human activity as well. Human activity and the specific landscape determine the concentration of nitrate in groundwater. For instance, very recent studies in areas with both shallow and deep water table (Biddau et al., 2019) found that in low areas not only a large fertilizer application, but also manure application and local sewage were related to higher nitrate concentration in shallow groundwater; however, in clay-dominated areas with low hydraulic conductivity and deeper water table, as is the case of the present paper, only low nitrate concentration was found. Unlike some western or southern European countries and regions worldwide with shallow water table and where farmers apply large amounts of fertilizers, specifically N-based fertilizers, Romania does not seem to have large-scale problems of nitrate pollution due to agriculture.

Because the sampling points are all in the built-up area of settlements, it is highly probably that the higher content values of cations and anions in water could be due to the domestic contribution occurred and facilitated through infiltration of water containing various amounts of pollutants coming from animal stables, unlined toilets dug 2-3 m in depth and that are closer to the water table and, more importantly, have their bottoms beyond the limits of the soil and clay deposits that possess low permeability. Another cause might be the leaching of solutes and polluted water from human households directly toward the water table, or even near the wells` tubes. This aspect should be clarified through future investigations.

As seen from the figures presented in the previous section, there was a large spatial variability among all the water properties analyzed. Nevertheless, comparing the current values of the groundwater content in anions and cations with its older values written on hydro-geological maps issued at the beginning of the 1970s years, even if this comparison is approximate because the water samples have not been collected from the same wells, the following observations have been noted:

a) the current mean values of the Cl^- (171 mg/l) and SO_4^{-2} (88 mg/l) are higher versus the old ones from the maps (***The Hydrogeological Map of the Danube Plain*), which ranged between cca. 20 and 100 mg/l between 20 and 50 mg/l, respectively, probably due to the subsequent contribution of such substances to the groundwater and attributed to human activities,

b) the current values of the Na^{+} cation content in the groundwater, 95.5 mg/l, is within the same large range from the years 1970s (***The Hydrogeological Map of the Danube Plain*), i.e. 50-100 mg/l, meaning relative stability and equilibrium between sources and transfers from the catchment,

c) the current mean value of the Mg^{+2} cation groundwater content (113 mg/l) exceeds substantially the old values (***The Hydrogeological Map of the Danube Plain*) that were approximately between 30 and 50 mg/l, but this observation should be viewed with caution due to the difference of the determination methods used,

d) the water mineral residue (1133 mg/l) remains within the same range that was in the 1970s, (***The Hydrogeological Map of the Danube Plain*) i.e. 1000-1500 mg/l.

The chemical composition of the soils from arable lands shows a higher leachable potential versus the soils of forest lands; the existence of some harmful anions to human health, like $N\text{-}NO_3$, from the wells situated within the built-up area of villages and settlements does not necessarily demonstrate their leaching from the arable land area toward the groundwater, due mainly to the low soil hydraulic conductivity of the Bt horizon, but rather the suspicions of deficiencies of hydrological isolation of the nitrate sources from human households, as already mentioned. Because there is groundwater pollution, mainly with nitrate, in the built-up area of villages with heavy-clay soils that are prevalent in this catchment and that possess low water permeability, this situation could probably be similar in other regions and might become a more spread feature in such environments in this country and other countries alike. Indeed, in a different environment, in the north-western part of Romania, Martonos & Sabo (2017) reported similar results with regard to the higher levels of sulfate (147- 260.5 mg/l) and nitrate (136.5 - 334.1 mg/l) in the water from wells.

These aspects, combined with other specific aspects should be further investigated including deeper drillings carried out in both arable and forest soils to groundwater.

5. CONCLUSIONS

Across the Glavacioc catchment, the surface water presents significantly higher pH values, being slightly alkaline, versus the groundwater that is neutral.

The water content in HCO_3^-, SO_4^{-2} and Cl^- is higher, but not significantly different in the groundwater versus the surface water. The prevalent ions in water are HCO_3^- and Mg^{+2}.

Large amounts of nitrates have been found in the groundwater samples from the wells in the built-up area of the villages, exceeding by about seven times the maximum allowed content value that is 50 mg/l. There are significant differences between the nitrate content from the groundwater, which is highly pollutant with this anion, versus the surface water of the Glavacioc River. Thus, for human consume the groundwater from wells is not suitable from the view point of nitrate content.

Groundwater contains higher amounts of Ca^{+2} and Mg^{+2} versus surface water, with non-significant differences between them for Ca^{+2} and significant differences for Mg^{+2}. This can be explained by the enriched subsoil in these two cations and rainfall water infiltration and flow toward groundwater. Water hardness is higher in the case of groundwater due to the Ca^{+2} content, compared to surface water and tap water alike. The Na^{+} content is higher in the groundwater versus the surface water, without significant differences between then. The K^{+} content is higher in the surface water, with non-significant differences between the two situations. Residual sodium carbonate (RSC) is lower than 0.5, and sodium adsorption ratio (SAR) is < 3 in both water types, and because the Na^{+} content is lower than 200 mg/dm^3, the groundwater has a normal content from this view point and can be used for irrigation.

As already seen, the groundwater contains higher anion and cation contents versus the surface water of the Glavacioc River, and for some of these components with significant differences. Even if the general direction of groundwater flow is toward the river, the river water shows a lower pollution level, probably because the fact that the polluted area in the built-up villages is small, punctual, specifically for nitrate, versus the larger field area around.

There are relationships between water mineral residue and some water chemical components: anions (HCO_3^-, NO_3^-, Cl^-, SO_4^{-2}), cations (Na^+, Mg^{+2}, Ca^{+2}, K^+) and electrical conductivity for both water types studied.

Because the sampling points are all in the built-up area of settlements, it is highly probably that the higher water content values of cations and anions could be due to the domestic contribution occurred and facilitated through infiltration of water containing various amounts of pollutants coming from animal stables, unlined toilets dug 2-3 m in depth and that are closer to the water table and, more importantly, have their bottoms beyond the limits of the soil and clay deposits that possess low permeability. Another cause might be the leaching of solutes and polluted water from human households directly toward the water table, or even near the wells` tubes. This aspect should be clarified through future investigations.

The chemical composition of the soils from arable lands shows a higher leachable potential versus the soils of forest lands, but due to the low soil hydraulic conductivity the flow of water and solutes toward groundwater is generally limited; the existence of some harmful anions to human health, like N-NO_3, from the wells situated within the built-up area of villages and settlements does not necessarily demonstrate their leaching from the arable land area toward the groundwater, but rather suspicions of deficiencies of hydrological isolation of the nitrate sources from human households.

Even if there are significant differences between some chemical components of groundwater and surface water, these both waters can be used for irrigation, but not for human consume until important measures are implemented to improve their quality.

Acknowledgements

The authors acknowledge the financial support received from the Romanian Ministry of Research and Innovation: Project PN-III-P1-1.2-PCCDI-2017-0721 – INTER-ASPA. The valuable contribution of Dr. Nineta Rizea and Dr. Venera Stroe for the chemical analyses of water samples is also acknowledged.

REFERENCES

Biddau R., Cidu R., Da Pelo S., Carletti A., Ghiglieri G. & Pittalis D. 2019. *Source and fate of nitrate in contaminated groundwater systems: Assessing spatial and temporal variations by hydrogeochemistry and multiple stable isotope tools*. Science of the Total Environment, Volume: 647: 1121-1136, Doi: 10.1016/J.Scitotenv. 2018.08.007.

Canoğlu M. C., Kurtulus B. & Razack M. 2019. *Soil–aquifer interactions and vadose zone modeling: An example from marais Poitevin (Western France),* Carpathian Journal of Earth and Environmental Sciences, Vol. 14, No. 1, p. 171 - 180; DOI: 10.26471/cjees/2019/014/069.

Damian F., Damian G., Lăcătușu R., Postolache C., Iepure G., Jelea M. & Năsui D. 2013. *The heavy metals immobilization in polluted soils from Romania by the natural zeolites use*. Carpathian Journal of Earth and Environmental Sciences, volume 8(4): 231-250.

Dumitru M., Simota C. & Calciu I. 2013. *Management of nitrates – Nitrate Directive*. Editura Solness. 423 pp. (in Romanian).

Dumitru S., Ignat P., Anghel A., Gherghina A. & Vrinceanu A. 2009. *Mapping the nitrate contamination levels in the groundwater in Timis County – A GIS approach*. Research Journal of Agricultural Science, vol. 41 (2): 98-103.

Florea N. 1976. Geochemistry and valorization of the waters from the North-Eastern Romanian Plain. Editura Academiei RSR. 201 pp. (in Romanian).

Florea N. & Munteanu, I., 2012. Romanian Soil Taxonomy system–*SRTS*. Edit. Sitech, Craiova, 206 pp. (in Romanian).

Geiger R. (1961) *Überarbeitete Neuausgabe von Geiger, R.: Köppen-Geiger / Klima der Erde*. (Wandkarte 1:16 Mill.) – Klett-Perthes, Gotha.

Gherghina A., Ignat P., Anghel A., Vrinceanu A., Eftene M., Panoiu I. & Dumitru S. 2010. *Relations between fertilizer management and landscape components on zones vulnerable to nitrates from the western part of the Romanian Plain*. Proc. of the 15th World Fertlizer Congress of International Scientific Centre for Fertlizers, 29 aug. – 2 sept. 2010, Bucharest. Editors Hera C., Dumitru M., Schung E., Dorneanu A., Haneklaus S., Popescu A., Anton I., Panoiu I. Editura Academiei Romane.

Grumeza N., Klepş C. & Tuşa C. 1990. *Evolution of groundwater level and chemistry from the irrigation systems related to the environment.* MAIA, DGEIFCA-ASAS, Centrul de Propagandă Tehnică Agricolă, București, 571 pp. (in Romanian).

Ispas G., Roba C., Bălc R., Coadă M. & Gligor D. 2018. *The quality of water and soil in Haneș mining area, Alba County, Romania.* Carpathian Journal of Earth and Environmental Sciences, Vol. 13, No. 2: 505 - 514; DOI:10.26471/cjees/2018 /013/043.

Lăcătușu R. 2017. **Agrochemistry**, Terra Nostra Publisher, Iasi, 440 pp. (in Romanian).

Lăcătuşu R., Lungu M., Rizea N. 2017. Global chemistry of soil processes, determinations, interpretations. Terra Nostra. Iași, 474 pp. (in Romanian).

Lăcătuşu R., Răuță C., Cârstea S., Ghelase I. 1996. Soil-Plant-Man relationships in heavy metal polluted areas in Romania. Applied Geochemistry. Vol. 11: 105-107.

Lăcătuşu R., Răuță C., Grigore C., Cârstea S., Ghelase I. 1993. *Geochemical and biogeochemical features of areas of hematuria in cattle in the Eastern Carpathian Mountains of Romania*. Environmental Geochemistry and Health. Vol. 15(1): 3-13.

Lăcătuşu R., Răuţă C., Ghelase I., Cârstea S., Kovacsovics B. 1994. *Local nitrate pollution of soils, waters and vegetable in some areas of Romania*. Transactions of 14th Arbeitstagung Mengen und Spurenelemente, Jena, Germany: 491-497.

Martonos I. M. & Sabo H. M. 2017. *Quality of drinking water supplies in Almaşu rural area (Salaj county, Romania).* Carpathian Journal of Earth and Environmental Sciences, Volume 12, Number 2: 371 – 376.

Mocanu A.M. 2005. *Nitrates a risk ? Study in the Olt county*. Editura SITECH, Craiova (in Romanian).

Nicula A.M., Roba C., Piştea I. & Roşu C. 2017. *Assessment of water quality from Brăteni Lake, Bistriţa-Năsăud county*. Carpathian Journal of Earth and Environmental Sciences 12(2): 365-370.

Paltineanu C., Chitu E., Mateescu E. 2011. *Changes in crop evapotranspiration and irrigation water requirements*. International Agrophysics. 25(4), pp. 369-373.

Paltineanu C., Chitu E., Mateescu E. 2012. *New trends for reference evapotranspiration and climatic water deficit*. 2012. International Agrophysics. 26(2), pp. 159-165.

Paltineanu C., Lăcătuşu R., Vrinceanu A., Vizitiu O., Lăcătuşu A. R. 2019. *Comparing soil physical properties in forest soils and arable soils within heavy-clay Phaeozems: an environmental case study in Romania*. Agroforestry Systems. Volume 92, DOI: 10.1007/s10457-019-00373-9.

Paltineanu C., Chitu E., Tanasescu, N., Apostol, G., Pufu, M.N. 2000. *Irrigation water requirements for some fruit trees specific to the Arges-Vedea river basin, Romania*. Acta Hort. 537: 113-119.

Paltineanu C., Mihailescu I.F., Seceleanu I., Dragota C., Vasenciuc F., 2007. *Aridity, drought, evapotranspiration and crop water requirements in Romania*. Editura Ovidius University Press, Constanţa, 319 pp (in Romanian).

Paltineanu C., Septar L., Gavat C., Chitu E., Oprita A., Moale, C., Calciu I., Vizitiu O., Lamureanu G. 2016a. *Characterizing Root Density of Peach Trees in a Semi-arid Chernozem to Increase Plant Density*. International Agrophysics, Volume 30(1): 67–74, DOI: 10.1515/intag-2015-0079.

Paltineanu, C., Septar, L., Gavat C., Chitu E., Iancu M., Oprita A., Moale C., Lamureanu G., Calciu I., Stroe V.M. 2016b. *Spatial distribution of apricot roots in a semi-arid environment.* Agroforestry Systems. Volume 90 (3): 469-478. DOI: 10.1007/s10457-015-9869-8.

**The Hydrogeological Map of the Danube Plain*, scale 1: 100000, from 1970-1971-1973-1974), the Geological Institute of Romania (in Romanian).

****Act no. 311/2004 for modification and completion of Act 458/2002 on the quality of potable water*. M.Of. al României, no. 582/30-06-2004 (in Romanian).

Received at: 16. 01. 2019
Revised at: 29. 03. 2019
Accepted for publication at: 02. 04. 2019
Published online at: 08. 04. 2019