Spatial distribution of groundwater quality in connection with the surrounding land use and anthropogenic activity in rural areas

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Water quality is essential for ensuring humane living conditions for inhabitants around the world. In this context, an important aspect that must be taken into consideration is the water quality in rural areas. Special attention must be given in such cases due to a large number of possible pollution sources, from industrial or agricultural, to wastewater resulted from human use of water supplies. This paper provided valuable information on the status of a number of groundwater sources (60 wells) throughout Targoviste Plain, Romania. An extended study of the spatial distribution of groundwater quality in connection with the surrounding land uses was achieved. The results obtained using fluorescence spectroscopy have been completed by chemical studies in order to better establish the influence of nearby land use on well water quality. It was concluded that external influences, such as soil type or land use, had a significant effect on the chemical content of the shallow groundwater that supplied the wells. High concentrations of different pollutants found in shallow groundwater are determined by anthropogenic activities, industrial an agricultural, conducted in rural villages and their surrounding areas. High concentrations of humic-like organic matter (OM) were observed in a sparsely populated region, with a forest located nearby, thus evidencing a terrestrial input to the water system. On the other hand, in the region where the highest concentration of protein-like OM was registered, the land was used for agricultural purposes.

Keywords: *water quality; fluorescence spectroscopy; chemical analyses; rural area.*

Introduction

One of the world's pressing problems is referred to as the "global water crisis", which does not always imply the lack of water. The quality of water to which people have access is an emergent issue. The problem of poor water quality represents a daily concern, especially in developing countries, being considered a parameter for establishing the social and economic development of the countries (Draghici et al., 2017; Diaconu et al., 2017). In developing countries, inhabitants of urban and peri-rural areas rely on water wells as sources of drinking water and agricultural use (Lapworth et al., 2012; Cartwright et al., 2019). Therefore, innovative monitoring methods (Wittenberg et al., 2019; Yang et al., 2019) have to be developed and regulated for the microbiological, chemical and physical assessment of water (Jang 2013; Rotaru and Răileanu, 2008; Pavelescu et al., 2013; Zhou et al., 2016; Othman et al., 2018; Soler et al., 2018; Sakizadeh et al., 2019; D'Aniello et al., 2019). Contaminants produced by different anthropogenic activities (Ionus, 2011; Boengiu et al., 2016; Shaad & Burlando, 2019; Diaconu et al., 2019b) such as nitrates and pesticides caused by fertilization of agricultural fields as well as untreated human and animal wastes may leach into the groundwater, altering the quality of the water sources (Palmiotto et al., 2018; Thomas and Famiglietti, 2015). This increases the risk of contracting diseases associated with pathogens originating from faecal sources, such as cholera, dysenteric and enteric fevers (Bain et al., 2014; Sorensen at el., 2015).

During the last couple of decades, the attention of scientists has been directed towards the study and development of a rapid technique for investigating the composition and dynamics of organic matter (OM) present in every type of aquatic environment. Recent studies (Hudson et al., 2007; Sorensen at el., 2015, 2018; Nowicki at el., 2019) emphasized the importance of using fluorescence spectroscopy for testing water quality and its potential to be used as a tool for monitoring the microbial activity in aquatic media. The results of their research suggested that the study of peak T, according to Coble nomenclature (Coble, 1996), can be linked to the presence of pathogens, thus providing a tool for accurate assessment of the aquatic system water quality. Furthermore, fluorescence spectroscopy has proved to be able to offer valuable and reliable information on the type of OM content present in various water sources, either of proteic or humic origin. This method allows the

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identification of different characteristic markers which suggest the presence of bacterial matter or the terrestrial influence on the studied water systems (Hudson et al., 2007).

This study aimed to provide scientific data for characterizing and evaluating the water quality of shallow groundwater from an extended rural area in Romania. To this purpose, 60 wells were chosen in order to cover an area of around 1,000 km2. The experimental results obtained using fluorescence spectroscopy have been correlated with chemical studies in order to better establish the influence of nearby land use on well water quality. The chemical tests performed on the samples targeted specific chemical compounds that pose a danger to human health. The novelty of this study consists of a large number of wells investigated spread throughout a large rural area in Romania. The information obtained upon analysing the water from wells spread on an extended area could provide insight on the characteristics of the groundwater in that region (Avram et al., 2018; Dontu et al., 2018). Thus, the premises for more extensive research regarding the water quality assessment in rural areas in Romania would be created.

Materials and methods

Site description

Targoviste Plain is situated in the South-central part of Romania (Dambovita County), with a surface of 1,061 km^2 and 200,000 inhabitants (60 % living in rural areas). In the rural side of Targoviste Plain wells are still being used as drinking water sources. The water quality provided by these wells must be monitored continuously due to contaminants resulted (Ionus 2011; Minea et al., 2016; Minea 2017) from domestic and agricultural activities (i.e., crops and livestock farming) and climatic factors (Official Report of the Ministry of Health, 2016; Marinică et al., 2016; Pravalie et al., 2016; Minea and Croitoru, 2017; Andronache et al., 2017; Romanescu et al., 2014; Dunca, 2018; van Engelenburg et al., 2018; Grigoraș & Urițescu, 2018 ; Gohar et al., 2019). Targoviste City is the only urban centre in the studied area with intensive industrial and commercial pollution. Targoviste Plain is defined mainly by meadows and broad terraces along the Ialomita and Dambovita Rivers, and by its gravels and sands content, covered by loess deposits. The altitude of the studied area decreases from north to south, from 400 m to 200 m. The phreatic layer is situated at depths of 1-3 m in the meadow, 4-6 m in the low terraces of Ialomita and Dambovita Rivers and 25-26 m in the high terraces of the Dambovita River. Anthropogenic involvement on both rivers (for example, dam reservoir, fish ponds, etc.) leads to modification of the hydrological regime with direct implications on the transit of alluvial deposits from the bedrock and on the supply of the aquifer (Sencovici, 2014). The predominant activity is agriculture (53% of the area is arable land, 9% grassland and meadow, and just 25% forest), the region is famous for vegetable crops (Sencovici & Costache, 2012; Costache et al., 2014; Costache&Sencovici, 2015; Dunea et al., 2018). The water samples originated from 60 wells located throughout the Targoviste Plain will be hereafter referred to as W0-W59 (Figure 1). Their association with the studied area is depicted in Table 1.

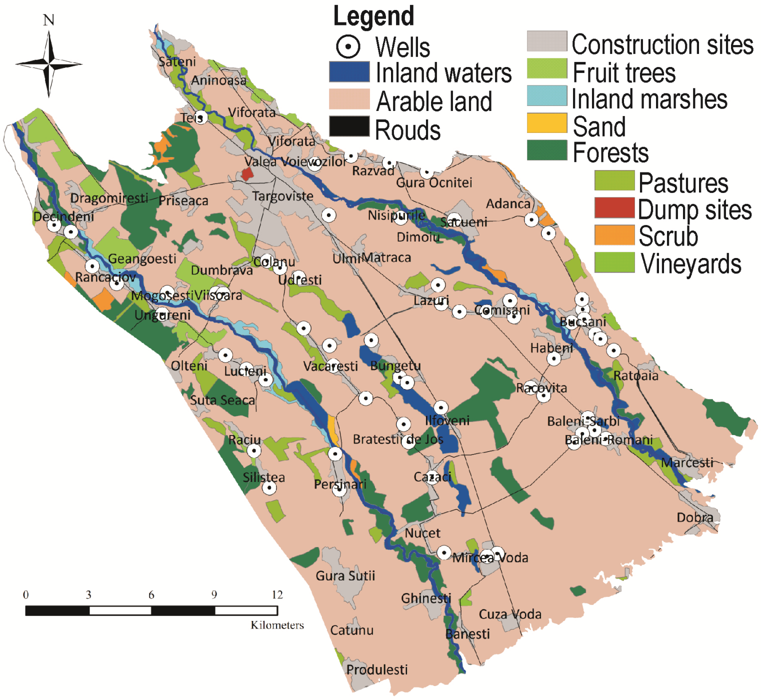

Figure 1. Map of samples location and the land use in the Targoviste plain

Table 1. Water supply status in Targoviste Plain

Investigated villages	Water Samples	Number of inhabitants	Total no. of dwellings	Dwellings with water supply		Dwellings without water supply	Dwellings with sewerage systems			Dwellings without sewerage systems
				Public network	Private supply systems		Public network	Private sewerage systems	Other situation	
Târgovişte city	W0	79,610	35,886	35,417	233	236	34,106	955	75	750
Baleni Sarbi	W1-W5	4,707	2,374	-	1,702	672	-	1,184	99	1,091
Bucsani	W6-W12	3,667	2,309	1,175	506	628	-	1,236	37	1,036
Habeni	W13	1,439								
Racovita	W14-W15	1,263								
Comisani,	W16-W19	3,480	1,835	743	717	375	-	1,068	3	764
Lazuri	W20-W21	1,920								
Decindeni	W22-W23	2,502	3,064	2,167	533	364	70	1,492	43	1,459
Mogosesti	W24	566								
Rancaciov	W25-W26	1,996								
Ungureni	W27	1,315								
Dragodana	W28	1,373	2,327	1,290	620	417	-	1,178	29	1,120
Gura Ocnitei	W29	3,160	2,748	1,546	611	591	148	1,522	38	1,040
Adanca	W30-W31	1,826								
Sacuieni	W32	1,830								
Lucieni,	W33	2,544	1,303	650	403	250	-	626	80	597
Nucet	W34	2,162	1,463	225	697	541	-	649	14	800
Cazaci	W35	1,396								
Ilfoveni	W36	499								
Persinari	W37-W38	2,750	934	-	483	451	-	252	12	670
Raciu	W39	1,566	1,505	1,018	233	254	-	609	102	794
Razvad	W40-W42	4,266	3,403	1,838	1,036	529	219	2,055	19	1,110
Valea Voievozilor	W43	3,023								
Teis	W44	2,489	2,247	1,498	405	344	174	1,129	130	814
Colanu	W45-W46	289	1,570	989	392	189	-	1,003	42	525
Nisipurile	W47	79								
Udresti	W48	216								
Viisoara	W49-W50	1,370								
Vacaresti	W51-W54	3,173	1,664	57	1,240	367	-	763	63	838
Bratestii de Jos	W55-W56	666								
Bungetu	W57-W59	1,407								

Sampling, sample preparation and analytical techniques

The water samples were collected in sterile plastic bottles and preserved in a cool box, at maximum 4°C, until analysis. All the samples were measured within 48 hours from the collection in order to minimise the risk of degradation. 60 wells (i.e. W0-W59) spread throughout Targoviste Plain were chosen for the study. The water analysis, including pH, electrical conductivity (EC), salinity and total dissolved solids (TDS), were performed by using pH/ISE meter inoLab® pH/ION 7320. Nitrate was determined using Dionex ICS-3000 Ion Chromatography system equipped with IonPac® AS9 analytical column with AG9 guard; the eluent was 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$; the flow rate was 2.0 mL/min, and the sample volume was 25µL. The analysis and quantification of elements (i.e. Cr, Fe, Co, Ni, Cu, Zn, Cd, and Pb) were performed by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) by using iCAP™ Qc device (Dulama et al., 2017). For ICP-MS analysis, the samples (about 15 mL) were digested with aqua reggia on a hot plate by using a TOPwave Microwave-assisted pressure system, according to the procedure proposed in previous studies (Radulescu et al. 2016; Radulescu et al., 2017). After the digestion process, the PTFE-TFM vessels with samples were cooled for 1 hour, and then the solutions were transferred with distilled water to 25 mL volumetric flasks. Finally, the clear solution samples were analysed by ICP-MS. The quantification of this technique was performed by a standard curve procedure. Metals calibration curves showed good linearity over the concentration range (0.1 to 10.0 mg L^{-1}), with R^2 correlation coefficients in the range of 0.996 to 0.999 (Chelarescu et al., 2017). Calibration was performed using standard aqueous solutions (Merck). The measurements were performed in triplicate mode. The relative standard deviation (RSD) was less than 5%.

Fluorescence spectroscopy was used in order to highlight the characteristics of OM. To this end, excitation-emission matrices (EEMs) were recorded using FLS-920 Edinburgh Instruments spectrofluorimeter which operates with a 450 W Xe lamp. Upon their recording, the spectra were analysed for distinct excitation/emission wavelengths. Specific fluorescence maxima were identified, using the peak picking method and associated with different types of OM present in the tested water samples (Coble, 1996). The EEMs were registered using excitation wavelengths in the 230-400 nm range and emission wavelengths between 250 and 500 nm, with steps of 5 and 2 nm, slits of 4 nm and an integration time of 0.2 s. The water Raman peak was recorded before each set of measurements in order to establish the stability of the instrument. The spectra were recorded in triplicate, and average values were used in the analysis.

Topographic, hydrological, hydrogeological and statistical information were processed and digitized using ArcGIS 10.4.1, the resulted thematic maps is based on a spatial database. The spatial distribution of the values was determined using non-parametric and linear geostatistical methods for estimating the spatial variation of the variables (Joumel, 1983; Chica-Olmo et al., 2014; Secu et al., 2015; Diaconu et al., 2019a).

Results and discussion

Chemical analyses

For a proper understanding of the water quality in the studied area, a number of chemical investigations were performed (Table 2). A slight acidic tendency could be noticed, as most of the samples had pH values slightly lower than 7. The lowest pH value (6.53) was registered for water sample W2, while the highest value (7.39) was recorded for sample W55. Given the fact that the pH values were in the 5-7 interval, it should not be considered as an impact factor for the differences observed in the fluorescence intensities. Reynolds & Ahmad 1995; Patel-Sorrentino et al., 2002; and Spencer et al., 2007, evidenced that when at pH values comprised in the 5-7 interval there were no significant differences in the fluorescent intensity signals. With regard to the electric conductivity, elevated values were measured for three samples, W6, W8 and W12, originating from the same village - Bucsani. High conductivity values indicated high concentrations of TDS (Figure 2), which were charged minerals in most parts. International agencies such as World Health Organisation (WHO) and the United States Environmental Protection Agency (EPA) established a maximum TDS level that must not be exceeded in drinking waters of 500 mg/l (www.epa.gov, WHO Guidelines for Drinking-water Quality, 1996). It could be observed that almost all of the water samples presented TDS concentrations higher than the maximum accepted value, which suggested the presence of charged ions, including salts and metal ions. As could be expected, the highest salinity values were also registered for the same well samples W6, W8 and W12. Our results revealed that in the majority of cases, high concentrations of hydrogen carbonate were obtained, compared to the value used as a standard by global organizations such as EPA and WHO. The lowest concentrations were recorded for three out of five samples collected from Baleni village (W1, W2 and W3). Past studies (Rylander, 2008) suggested that waters with concentrations of hydrogen carbonate higher than 110 mg/l are more beneficial to human health.

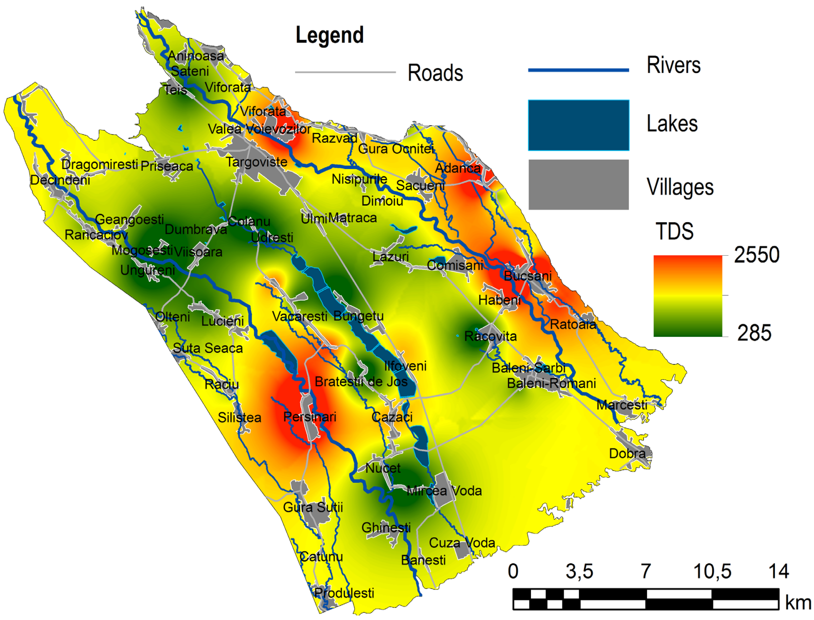

Figure 2. Spatial distribution of TDS in the study area

With regards to the concentrations of nitrates, sulphates, chlorides, calcium and magnesium from the water samples, the registered values were compared with the maximum allowed values, according to the Romanian and European Committee regulations (Romanian Law no. 311 from 28/06/2004; European Committee Directive 2006/118/CE). The results obtained indicated that well W18 registered the minimum Na, Ca, Mg, K, Sr and Ba concentrations, while W38 had the maximum values for Mg, Ca and Sr concentrations out of all the recorded values. These areas are situated in the proximity of vineyards. Certain types of grapes used in the wine industry need soil with different concentrations of nutrients. This could explain our findings, the mass cultivation for obtaining wines being responsible for the alteration of soil composition and thus of the groundwater quality parameters. The greatest Ga, In and Tl concentrations were recorded for well W6. An explanation for these results was the exploitation practices in the surrounding area. Beside agricultural practices, the region surrounding Bucsani was known for oil and natural gas extractions. Therefore, the presence of heavy metals in the groundwaters was tightly linked to the human activities nearby, among which was the manufacturing of mechanical components.

The chemical analysis revealed that all the sulphate and chloride concentrations were much lower than the maximum allowed values, the highest being 31.25 mg/L (W15) and 98.75 mg/L (W6) respectively. In the case of nitrate concentrations, the majority of the registered values were below the maximum allowed by law. However, for sample W2 it was recorded a concentration of nitrates of 60.4 mg/L, this being the highest value. Such values could signify a potential of exposure of the population to the risk of developing methemoglobinaemia in new-borns and adults with deficiencies of glucose-phosphate dehydrogenase. Given the fact that W2, W15 and W6 were found in regions characterized by arable land and construction sites, it was assumed that the high values for the sulphate, chloride and nitrate compounds were determined by the agricultural uses of the land (mainly corn, wheat and sunflower crops).

The spatial distribution of nitrate concentrations was presented in Figure 3a. According to a study performed by the World Health Organization (WHO), the natural nitrate concentration in groundwater under aerobic conditions could reach a few milligrams per litre, but must not exceeding 10 mg/l, depending on the soil type and the geological background (WHO Guidelines for Drinking-water Quality 2011). However, as a consequence of different agricultural activities, the nitrate concentration may increase by 100%, an extreme example being an agricultural area from India, where the nitrate concentration from groundwater reached 1,500 mg/L (Jacks and Sharma 1983; Nitrate and nitrite in drinking-water WHO, 2011). Intensive agricultural practices in the area might explain the relatively high levels of nitrate represented in Figure 3a. Although nitrate content in water can have a significant influence on human consumers, there are other threats that can be found in the groundwater supplies. Among these dangerous substances, heavy metals must be mentioned due to their cumulative effect. Lead is a cumulative poison, which has a strong effect, especially on children as well as on pregnant women and their fetuses (Lead in Drinking-water – WHO 2011). It is considered that an intake of a maximum of 5 µg/l from drinking water should not pose immediate health issues. In this context, it could be observed in Figure 3b that some areas were more affected than others, especially the ones corresponding to samples W1-W5. Comparing the two maps presented in Figure 3a and Figure 3b, it could be noticed that the same approximate area had high levels of lead and nitrate, possibly coming from industrial chemical waste. We could suppose that previous anthropogenic activities caused high levels of lead and nitrate now found in the groundwater system.

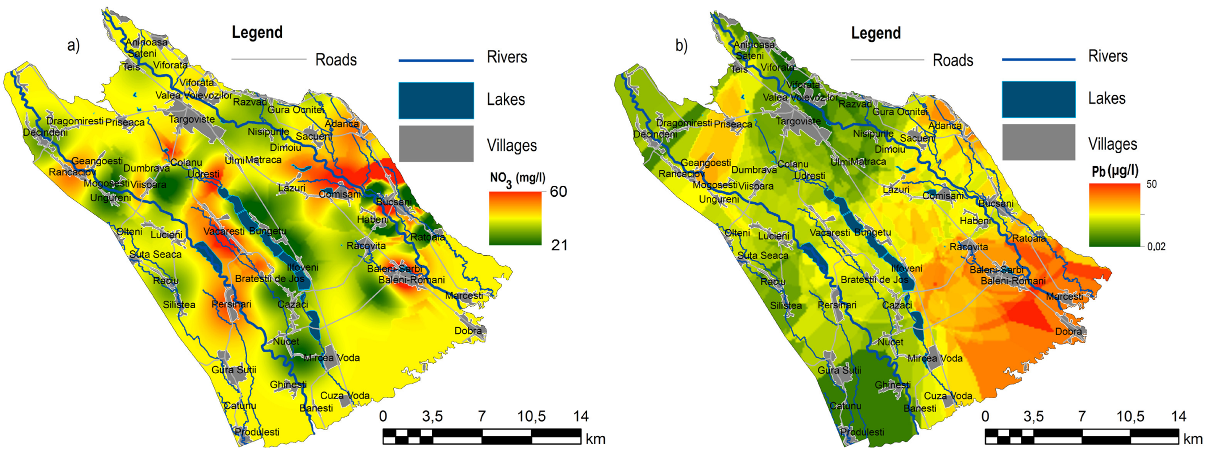

Figure 3. Accumulation of nitrates (a) and lead (b) in the water samples

Table 2. Information on sampling location and hydro chemical characteristics

n=60	Depth of hydrostatic level (m)	Sampling depth (m)	Temperature (°C)	pH	Conductivity (μS/cm)	Salinity (‰)	TDS (mg/L)	Cr (μg/L)	Fe (μg/L)	Co (μg/L)	Ni (μg/L)	Cu (μg/L)	Zn (μg/L)	Cd (μg/L)	Pb (μg/L)
Mean	6.02	9.04	13.58	6.88	1,397.98	0.69	680.00	49.93	341.04	0.93	37.40	13.44	44.06	0.21	18.86
Standard Error	0.65	0.72	0.15	0.02	99.36	0.05	51.31	1.69	19.06	0.05	2.62	1.09	4.41	0.07	1.99
Median	4.75	7.15	13.50	6.87	1,225.00	0.60	590.00	51.33	303.95	0.83	30.24	10.12	34.21	0.10	15.88
Mode	5.00	4.50	13.00	6.95	1,244.00	0.60	565.00	63.19	556.21	1.31	68.13	20.14	35.03	0.10	24.14
Standard Deviation	5.03	5.55	1.16	0.16	769.60	0.41	394.12	12.28	138.72	0.35	19.06	7.94	32.09	0.50	14.51
Sample Variance	25.32	30.78	1.35	0.03	592,286.15	0.16	155,327.14	150.72	19,244.46	0.12	363.35	63.00	1,029.61	0.25	210.61
Kurtosis	2.99	1.84	-0.34	1.05	10.50	10.58	10.88	4.08	-0.05	3.12	0.44	1.18	0.00	29.11	-0.42
Skewness	1.61	1.37	0.49	0.63	2.95	2.97	3.02	-1.42	0.56	0.90	1.00	1.32	1.07	5.07	0.76
Range	24.00	24.50	4.50	0.86	4,421.00	2.30	2,265.00	70.12	682.54	2.24	87.84	34.84	126.42	3.32	50.46
Minimum	1.00	3.00	12.00	6.53	599.00	0.30	285.00	0.12	14.32	0.04	0.10	0.17	2.94	0.00	0.02
Maximum	25.00	27.50	16.50	7.39	5,020.00	2.60	2,550.00	70.24	696.86	2.28	87.94	35.01	129.36	3.32	50.48

The accepted maximum concentrations of different metal ions, in groundwaters are regulated by national and international laws enforced by different agencies (Ministry Order 621/July 2014, Romanian Law no. 311 from 28/06/2004; European Committee Directive 2006/118/CE and U.S. Environmental Protection Agency). The spatial distribution of some heavy metals concentrations was shown in Figure 4. Our studies showed that the tested samples have Cr concentration close to the maximum accepted value, with the lowest concentration registered for sample W18. Co, Cu, Cd and Pb concentrations remained within the allowed range, while the iron concentrations were close to the maximum allowed limit. Also, 95% of the samples presented high concentrations of Ni, the highest value being registered for sample W37, over three times greater than the maximum allowed value. The high concentrations of Ni which were found in groundwater bodies could be a result of ore-bearing rocks found in the vicinity of the water sources, this supposition being also backed-up by research undertaken by WHO concerning the influence of ore-bearing rocks on the environment (WHO 2011). With regards to the Zn concentrations, in three cases, W26, W42 and W56, the registered values exceeded the maximum allowed limit. The high concentrations of this particular compound could have originated from the agricultural and industrial activities in the area, such as oil extraction and refineries.

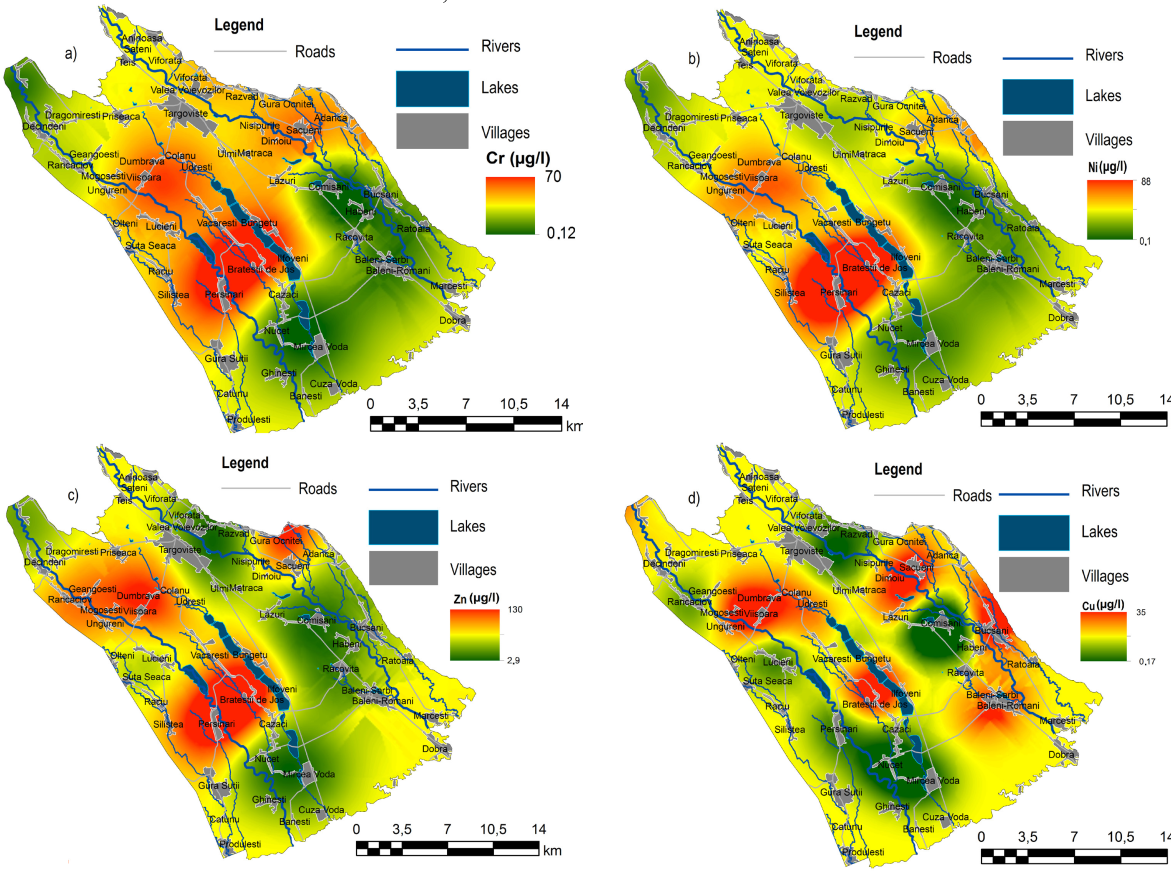

Figure. 4. Heavy metals concentrations (μg/l) present in the water samples (a) - Cr (μg/l); (b) - Ni (μg/l); (c) - Zn (μg/l); (d) - Cu(μg/l)

Fluorescence spectroscopy

Fluorescence spectroscopy was used in order to identify the presence of protein-like and humic-like components of OM. A graphical illustration of the geographical distribution of the fluorescence spectroscopy data is presented in Figure 5. The protein-like signature in the fluorescence spectra is given by peaks T (tryptophan-like) and B (tyrosine-like), while the humic-like marker is exhibited by peaks A, C and M (Coble, 1996). Peak T was recorded in the region λ_{ex}=230-240 nm/λ_{em}=325-345 nm, while peak B was determined in the region λ_{ex}=230-240 nm/λ_{em}=300-310 nm. In the case of humic-like substances, the wavelengths domains were λ_{ex}=230-250 nm/λ_{em}=405-430 nm for peak A, λ_{ex}=300-350 nm/λ_{em}=410-435 nm for peak C (Carstea et al., 2013) and λ_{ex}=312 nm/λ_{em}=380-420 nm for peak M (Carstea et al., 2013; Hudson et al., 2007).

The acquired data revealed that the humic signature (peaks A and C) was more intense than the proteic one for most of the samples. The highest values registered for these peaks originated from the sample wells W26 and W41 located near forests or pastures, while the lowest values corresponded to the water collected from W38 where arable lands and construction sites could be found. Peak M, usually found in areas that have recent biological activity (Coble, 1996) had the highest intensity for sample W22 situated on the green area, while the lowest value corresponded to a well situated in an area where the land was predominantly used for vegetable plantation and greenhouses. Lapworth et al. (2012) showed that greater quantities of OM reach shallow water tables (~1.5 m below ground) compared to deep aquifers. Apart from a natural OM contribution, nutrients from the agricultural activities could infiltrate into shallow water beds through rainfall and surface runoff.

Peaks T and B were commonly associated to microbial activity (Hudson et al., 2007), and recently, Sorensen et al. (2015) found a relationship between peak T and enteric pathogens in drinking water sources. This relationship depended on the water source proximity to toilets, the depth of the well, the type of bedrock and season. The highest intensities for peaks T and B were registered at the water sample W26. According to Sorensen et al. (2016), 91% of water sources contaminated with thermotolerant coliforms were located within 10 m of a toilet. Pit latrines and septic tanks are commonly used in the rural area of the Targoviste Plain, and therefore it could explain the results.

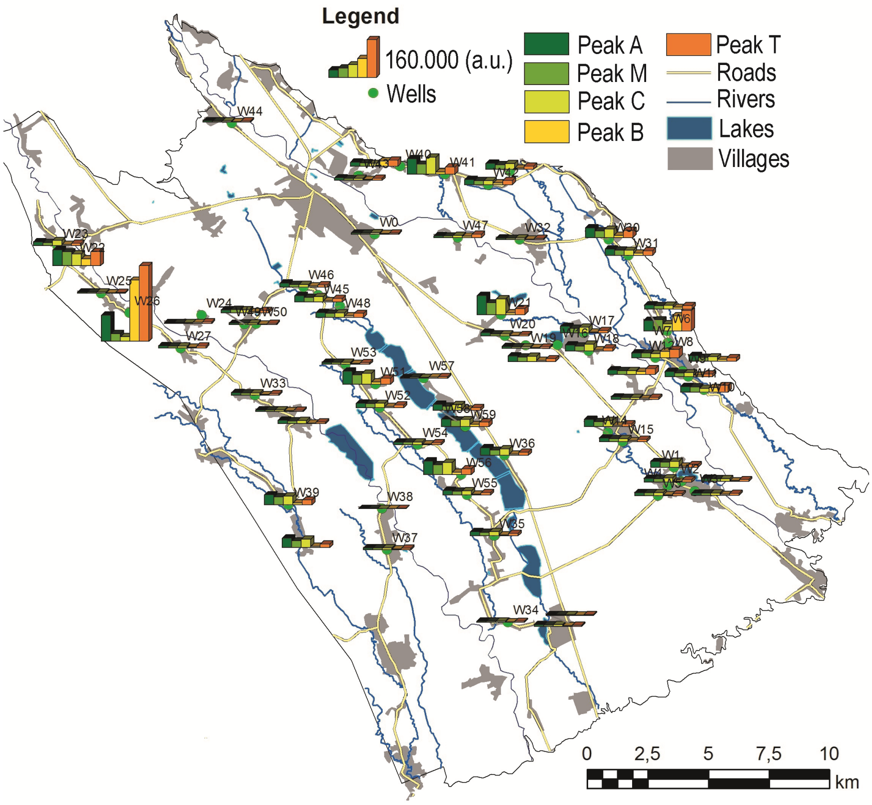

Figure 5. The distribution of fluorescence peaks associated with protein-like and humic-like substances

For determining the predominant OM fraction of each water sample, the ratio between peaks T and C was evaluated (Figure 6). As mentioned before, the results suggested that the majority of the tested samples were predominantly comprised of humic or fulvic-like material with the T/C ratio less than 1. Only twelve out of 60 samples presented values higher than 1 for the T/C ratio, suggesting that in the case of these samples, the microbial signature was more significant. We observed that the sites where the water samples presented the highest T/C values (W6, W12, W24, W26, W40 and W57) were located in the vicinity of mostly arable lands. In the region where the samples were collected, there were also a few construction sites, but the arable lands were predominant. This could explain the contamination of the groundwaters with soil enriched with organic fertilizer which may have led to an increase of bacterial activity in the soil. Another possible explanation could be the use of organic fertilizer, thus causing higher fluorescent intensities for protein-like peaks. This assumption was supported by studies which suggested that in recent years, the focus has been directed toward organic farming, using animal waste among other practices (Lori et al., 2017). In the case of wells W6 and W12, there was another possible explanation for the high intensities registered for peaks T, B and M. These wells were located in an area with former oil exploitation activities. Previous studies (Carstea et al., 2012) demonstrated that water samples containing traces of petroleum had characteristic fluorescence signatures, giving rise to higher intensities of peaks T, M and B. Therefore, with regard to samples W6 and W12, the most probable explanation for high values of the peaks B, T and M was the presence of petroleum in the groundwater samples. This hypothesis was supported by the chemical analysis performed on samples W6 and W12. Also, there were high concentrations of heavy metals usually found in the composition of petroleum products (Akpoveta and Osakwe, 2014). Moreover, sample W6 had the highest concentrations of Co and Cd from all the tested samples, while the concentration of Pb from sample W12 was high. These results, along with the knowledge of the previous use of the land suggested that the intensity of peak T might have been influenced by petroleum content, microbial content, or even both.

The lowest values of T/C ratio (T/C <0.5) were registered for samples W14, W17, W21, W23, W56 and W58. In these cases, the surrounding environment was comprised of forests (W14 and W56), pastures (W17, W21, W23 and W58) and inland waters (W17 and W58). Well W57, which had a prevalent microbial-like signature, was closer to the forest, while well W58, which exhibited predominant humic-like markers, was situated in a region of the same village, farther to the forest land. It could be concluded that forests, pastures and inland waters had an important contribution on the groundwater systems, in these cases, the humic-like signature found in the fluorescence spectra being more prominent than the microbial-like markers.

In the region where the highest concentration of protein-like OM was registered, the lands were used for agricultural purposes (arable land and a vineyard) as depicted in Figure 1. In contrast, the area where the T/C ratio was lowest, thus suggesting a high concentration of humic-like OM, a region with reduced human interaction was remarked, a forest being located in there.

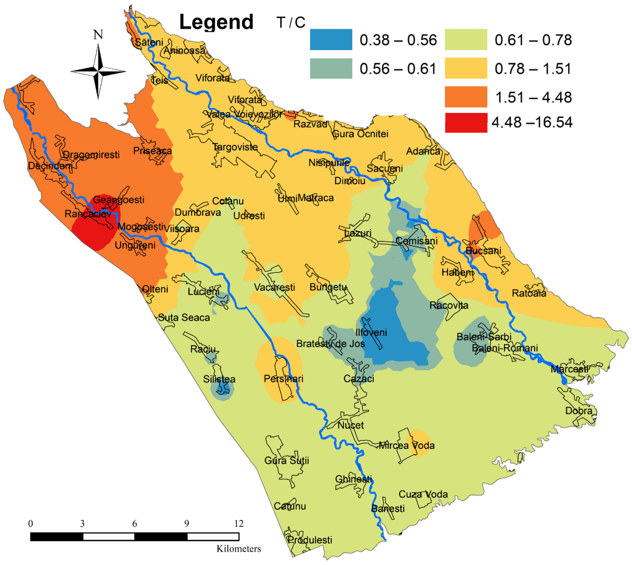

Figure 6. T/C ratio, evidencing the protein-like and humic-like character of the studied wells.

In order to evaluate the degree of OM hydrophobicity, the emission wavelength of peak C was determined for each sample (Figure 7). According to the studies conducted by Baker et al. (2018) low wavelengths, registered in the 400-420 nm range, are associated to relatively hydrophilic OM, while high wavelengths, ranging from 430 nm to 450 nm, are characteristic to waters with hydrophobic OM tendencies (Baker et al., 2008). Most of the samples presented a tendency towards hydrophilic OM. Mixed hydrophilic – hydrophobic and mostly hydrophobic matter was predominant in areas with fruit trees, forests, meadows and vineyards.

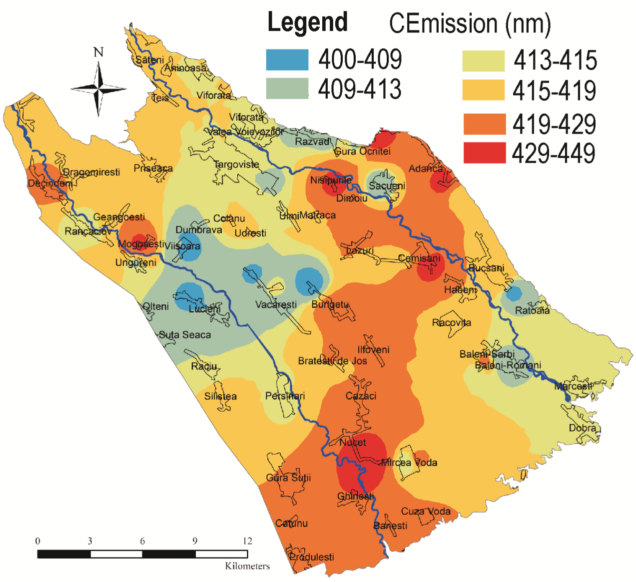

Figure 7. The distribution of the hydrophobicity degree of groundwater OM.

Table 3. Correlation matrix of the selected 23 Physico-chemical parameters determined for the left bank of Ialomita River.

	Conductivity	Salinity	TDS	SO_4	HCO_3	Na	Mg	Fe	Co	Ga	Sr	Cd	In	Ba	Tl	Pb	PeakA (a.u.)	PeakM (a.u.)	PeakC (a.u.)	PeakB (a.u.)	PeakT (a.u.)	CEmission (nm)	T/C
Conductivity	**1**																						
Salinity	**1**	**1**																					
TDS	**1**	**1**	**1**																				
SO_4	0.59	0.59	0.59	**1**																			
HCO_3	0.27	0.28	0.28	0.63	**1**																		
Na	0.33	0.33	0.34	0.64	**0.95**	**1**																	
Mg	0.64	0.62	0.64	0.36	0.19	0.30	**1**																
Fe	0.40	0.38	0.40	0.23	0.30	0.42	**0.84**	**1**															
Co	**0.75**	**0.74**	**0.76**	0.31	0.39	0.48	**0.78**	**0.76**	**1**														
Ga	**0.85**	**0.85**	**0.85**	0.55	0.51	0.56	0.67	0.46	**0.80**	**1**													
Sr	**0.87**	**0.86**	**0.87**	0.43	0.17	0.34	0.67	0.56	**0.82**	**0.73**	**1**												
Cd	**0.87**	**0.87**	**0.87**	0.55	0.54	0.62	0.63	0.51	**0.88**	**0.93**	**0.81**	**1**											
In	**0.84**	**0.84**	**0.85**	0.50	0.53	0.62	0.65	0.58	**0.93**	**0.90**	**0.83**	**0.99**	**1**										
Ba	0.61	0.61	0.62	0.24	0.44	0.48	0.60	0.68	**0.86**	0.67	**0.73**	**0.76**	**0.83**	**1**									
Tl	**0.86**	**0.86**	**0.87**	0.49	0.52	0.58	0.62	0.52	**0.90**	**0.91**	**0.84**	**0.98**	**0.99**	**0.85**	**1**								
Pb	-0.08	-0.09	-0.09	-0.04	-0.21	-0.22	0.28	0.05	0.02	-0.03	-0.04	-0.08	-0.11	-0.14	-0.13	**1**							
PeakA(a.u.)	0.17	0.18	0.17	0.11	0.21	0.21	0.20	0.12	0.09	0.29	-0.03	0.28	0.24	0.17	0.24	-0.24	**1**						
PeakM(a.u.)	0.43	0.44	0.43	0.31	0.43	0.46	0.40	0.33	0.41	0.57	0.27	0.59	0.57	0.46	0.56	-0.31	**0.92**	**1**					
PeakC(a.u.)	0.02	0.03	0.02	-0.07	0.00	-0.02	0.04	-0.06	-0.08	0.13	-0.21	0.10	0.05	-0.02	0.05	-0.17	**0.96**	**0.80**	**1**				
PeakB(a.u.)	**0.78**	**0.78**	**0.78**	0.50	0.57	0.63	0.51	0.50	**0.81**	**0.81**	**0.78**	**0.90**	**0.92**	**0.86**	**0.94**	-0.36	0.33	0.65	0.12	**1**			
PeakT(a.u.)	**0.77**	**0.77**	**0.78**	0.51	0.55	0.62	0.58	0.53	**0.77**	**0.83**	**0.71**	**0.89**	**0.90**	**0.80**	**0.91**	-0.34	0.55	**0.81**	0.34	**0.96**	**1**		
CEmission (nm)	0.05	0.05	0.05	0.25	0.09	0.01	0.21	0.00	-0.08	0.12	-0.17	0.01	-0.08	-0.16	-0.05	0.62	0.04	-0.02	0.06	-0.18	-0.11	**1**	
T/C	**0.72**	**0.72**	**0.73**	0.40	0.36	0.40	0.45	0.47	**0.74**	0.65	**0.82**	**0.73**	**0.79**	**0.86**	**0.83**	-0.34	-0.03	0.30	-0.22	**0.89**	**0.77**	-0.27	**1**

Due to the various industrial activities that occurred in the surrounding area of the villages situated on the left bank of the Ialomita River, a correlation between the chemical analysis and the fluorescent data has been made and is presented in Table 3. This particular region was subjected to oil exploitations, and there might be some residual pollution related to this type of land use. On the other hand, there are villages, such as Razvad (W40-W42) and Bucsani (W6-W12) where the water quality of the wells could have been impaired due to the diverse industrial influences in the region. From agricultural practices to waste resulted from the pharmaceutical industry and the manufacture of mechanical equipment, the soil and groundwater system were exposed to contamination with various chemical compounds, dangerous for human consumption.

As it could be observed, there was a good correlation ($r>0.7$) between peaks T and B and some heavy metals (Co, Ga, Sr, Cd, In, Ba and Tl). It was interesting to mention that the best correlation was registered between peaks T and B and Cd, In and Tl. These heavy metals are a major concern when found in drinking water sources, and their strong relationships with specific fluorescence signatures could signify that fluorescence spectroscopy could be used as a forefront investigation for determining the quality of groundwater sources, although more research should be undertaken before affirming with absolute certainty that there is a direct link between them. The concentrations of Tl, In and Cd in this area could be linked to the activities performed in the nearby plant that is specialized in manufacturing mechanical components.

It is important to monitor the groundwater quality, especially in regions where people rely on this kind of water supply for their daily use. The present studies generated a platform for further data, regarding the ability to monitor and identify potential health threats that people might come in contact to. The increased number of studied wells as well as the extent of the area which was investigated, bring new light into the mechanisms that influence the contamination of groundwater systems by external influences, such as soil or land use activities. In this context, our results offered new information on the status of various wells distributed across an extended rural area that relies mostly on well water for daily consumption of household and agricultural endeavours. It is necessary to maintain permanent control of these wells, considering the agricultural activities and exploitations undertaken in the surrounding area, which can lead to alteration of the water quality.

Conclusions

This study presented an evaluation of well water quality from private and public wells located in a rural area from Romania, with industrial and agricultural inputs. The study of chemical parameters and fluorescence indicators was useful to illustrate the impact of soil particularity and anthropogenic activities on groundwater quality. Environmental information regarding the land use in the vicinity of the wells suggested that due to agricultural activities and former oil exploitations, the water quality decreased, in some areas posing a real danger to the population who uses the wells for drinking water.

It was observed that external influences such as soil and land use had a major effect on the chemical content of the groundwater that supplies the wells from Targoviste Plain. Thus, in 95% of the cases, high concentrations of Ni were detected, as a result of ore-bearing rocks found in the vicinity of the water sources. Moreover, the present and former exploitations of the land could have determined an excess or a lack of chemical compounds in the water. An example was the impact of vineyards on the water quality parameters, different types of grapes needing different types of nutrients, influencing the concentration found in the soil and the underground water. In the same manner, the water coming from wells found in regions where oil extractions are common practices had traces of heavy metals.

Low concentrations of hydrogen carbonate, and high concentrations of lead (50.48 µg/L) and nitrate were found as the result of anthropogenic activities in construction sites and arable lands. High registered values for the sulphate, chloride and nitrate compounds were determined by the soil enriched with organic fertilizer, which also may have led to an increase of bacterial activity in the soil. In the region where the highest concentration of protein-like OM was registered, the lands were used for agricultural purposes, while a high concentration of humic-like OM was present in a region with reduced human interaction, a forest being located there. It could be concluded that there was a strong connection between land uses surrounding wells in rural areas and the water quality they provided. Moreover, the large number of analysed wells spread throughout an extended area provided an overall image on the status of surface underground water sources in a particular area of Romania. These findings could create the premises for even larger experiments in order to gain an accurate understanding of the mechanisms that influence water quality in rural areas.

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