Distribution of Mineral Nitrogen Compounds in Groundwater in Vaslui County (Romania)

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Groundwater quality parameters include simultaneous determination of inorganic nitrogen species, in the oxidized (NO_2^-, NO_3^-) and reduced (NH_4^+) forms, together with many other physical and chemical parameters. The objective of this study was to monitor the quality of groundwater in the northern and central part of Vaslui County (Romania), with a particular interest about nitrogen species. It was shown that for two series of groundwater samples taken from the same locations, but in different periods (December 2013 and May 2014), values the maximum Romanian legal limit (NH_4^+, NO_2^-) of concentrations were measured for ammonium ions (0.5 mg·L^{-1}), especially, but also for nitrite ions (0.5 mg·L^{-1}). These exceeding values were even more noticeable with samples taken in the spring of 2014, after a mild winter with low amount of precipitations. At that moment were no values of the nitrate ions exceeding the maximum allowed value to justify an intervention of local authorities. An investigation of the agricultural and livestock activities occurring in the area in which the samples were collected outlined a highly probable correlation with the detected conspicuous ammonium concentrations.

Keyword: *ammonia, nitrite, nitrate, groundwater, quality parameter*

It is well known that groundwater is a valuable natural resource which must be protected against deterioration and chemical pollution. Nowadays, groundwater importance focuses on its use as a source of drinking water, but also in the industry and agriculture. The analysis of nitrogen compounds in the natural and/or drinkable water represents a complex problem of environmental protection. Nitrogen forms soluble in water are mineral nitrogen (ammonium ions - NH_4^+, nitrite - NO_2^- and nitrate - NO_3^-, respectively) and organic nitrogen [1-3].

The main polluting activities in Barlad River Basin, Romania, are linked to agriculture, forestry activities and constructions. Farming in some areas ensures the premises of groundwater or surface water pollution with nitrogen compounds through excessive use of pesticides or inappropriate irrigation. Agriculture contributes to pollution with significant quantities of nitrate ions, resulted from demineralization or fermentation of household waste, the mineralization of chemical fertilizers, or the mineralization of soil humus [4-9].

The presence of ammonium ions, NH_4^+ represents a form of recent pollution of groundwater. The most important sources of ammonium ions are agriculture and chemical fertilizers, then animal farm waste and the activity of treating household waste. In the presence of soluble oxygen and specific autotrophic bacteria (*Nitrosomonas*), the ammonium ion oxidizes into nitrite ion and nitrate ion [10]. Nitrite ion is the intermediate stage of ammonium ion oxidation and it forms during the biodegradation of organic nitrogen compounds in water or of various fertilizers in the soil.

Their presence in the drinking water is not allowed taking into account the capacity of nitrite ions to form methemoglobinemia [11], and also its capacity to generate carcinogenic compounds in the presence of amines [12]. The presence of nitrate ions in water and soils is an essential problem to human health. When their concentrations in the groundwater are higher, there is a real danger of drinking water sources contamination, of eutrophication of surface waters and population endangerment [7]. As both ions (nitrate and nitrite) are associated with the formation of carcinogenic nitro-amines, their presence in the groundwater can lead to serious dysfunctions of human health - cyanosis, stomach problems or various types of cancer and is limited under the law in every country. Some authors claim that nitrate ions act as a promoter of human cancer [12, 13].

The anthropogenic interventions on hydrographic basins causing the content of nitrogen compounds often higher than the *maximum allowed limit* (MAL) for NO_2^- = 0.5 mg·L^{-1}, NO_3^- = 50 mg·L^{-1} and NH_4^+ = 0.5 mg·L^{-1} [14].

Groundwater is an important source of drinking-water in many countries, and is the main source of drinking-water in Europe [15]. The WHO [16] has established a drinking-water guideline value (short-term exposure) for nitrate and nitrite of 50 mg·L^{-1} and 3 mg·L^{-1}, respectively, to protect against methaemoglobinaemia in bottle-fed infants. The Australian Government [17] drinking-water guideline has adopted the WHO guidelines for infants under 3 months of age. However, the guideline is up to 100 mg·L^{-1} nitrate for adults and children over 3 months of age.

The Canadian drinking-water (health-based) guideline for nitrate is 45 mg·L^{-1}. Where nitrate and nitrite are determined separately, concentrations of nitrite should not exceed 3.2 mg·L^{-1} [19, 19]. In the USA, the Environmental Protection Agency maximum contaminant level for nitrates (measured as nitrogen) is 10 mg·L^{-1} (45 mg·L^{-1} nitrate); that for nitrites (measured as nitrogen) is 1 mg·L^{-1} [20].

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Because in the last years, there were some cases of methemoglobinemia in the area [21], we have analyzed the concentrations of nitrogen compounds in groundwater from Vaslui County, Romania. In the most of rural areas from Romania, groundwater is the main source of drinking water because, on the one hand, sources of groundwater are rich and, on the other hand, geological conditions favour such a situation.

The objective of the present paper is to identify concentrations of ammonium, nitrites and nitrates, respectively, in the groundwater in the northern and central part of Vaslui County, Romania. The study involved 20 samples taken in the autumn of 2013 (*S1 samples*) and in the spring of 2014 (*S2 samples*) from the same locations situated in the proximity of rural communities, taking into account the water table in the area in both the cold and warm season.

Located in the eastern part of Romania, between Zeletin and Prut rivers, Vaslui County overlaps the superior and middle Barlad River (tributary of the Siret River) and a related sector of the Prut River basin and its right tributary, Elan. From geological point of view, the territory is developed on sand-clay and limestone deposits of Sarmatian and Meotian [22]. In the major riverbed of Barlad River and on its terraces there are ravels, sands, sandy-clay silts deposits of Quaternary age (Pleistocene and Holocene) [23]. In the major riverbed Racova basin there are Quaternary sandy-clay silts. In the north of the territory, the groundwater lenses are stationed sandy-clay and clay deposits. The aquifer layers are stored in sedimentary formations with a depth of 5-30 meters stationed in the southern half of the territory [23, 24].

Pleistocene deposits are largely exposed in Moldova Platform (Eastern Romania) on the Barlad Valley, on the terraces of this river and its tributaries. One of the most illustrative Pleistocene successions can be studied in Simila open pit, where in the last decade large amounts of sand and gravel were extracted for construction [25]. The Sarmatian deposits are disposed concordantly over the Badenian deposits, which spread over the north-eastern part of the Moldavian Platform. Vaslui County is an emblematic paleontological site for the whole Romanian vertebrate palaeontology [25]. One site is for instance of interest for Miocene vertebrates, named Gherghesti 1 (fig.1) where was discovered a fragmentary skeleton of *D. proavum* [26, 27].

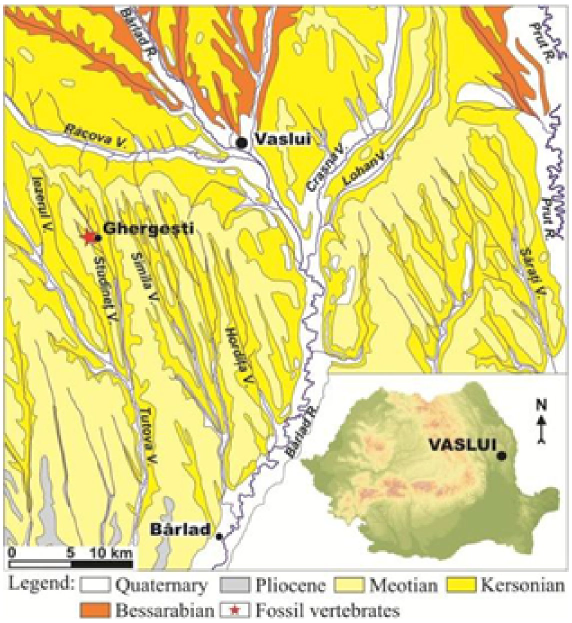

Fig. 1. Geological map of study area [23]

The surface of the deep groundwater body is 12.531 km^2 [28, 29]. The probing drills made in that water body investigated, all the aquifer networks encountered and the flow rates recorded during experimental injection, represent the cumulated value of the aquiferous possibilities in different hydro-structural units [28, 29]. With the largest area of the Siret River tributaries (over 7.220 km^2), the hydrographic Barlad Basin river covers over 45% of Moldavia Platform, located between Siret and Prut rivers. The Barlad Basin River is part of the Siret Basin River, accounting for 17.1% of its surface [30].

Experimental part

Materials and methods

20 water samples were taken from the same locations in December 2013 (*S1 samples*) and May 2014 (*S2 samples*) (fig. 2). The quantity for the initial sample was 500 mL, these were preserved with a small amount of hydrochloric acid solution and transported to the lab for analysis. The distribution of samples aimed at the investigation of the effect of agricultural activities (10 samples), livestock farms (6 samples) and garbage dump sites (4 sample).

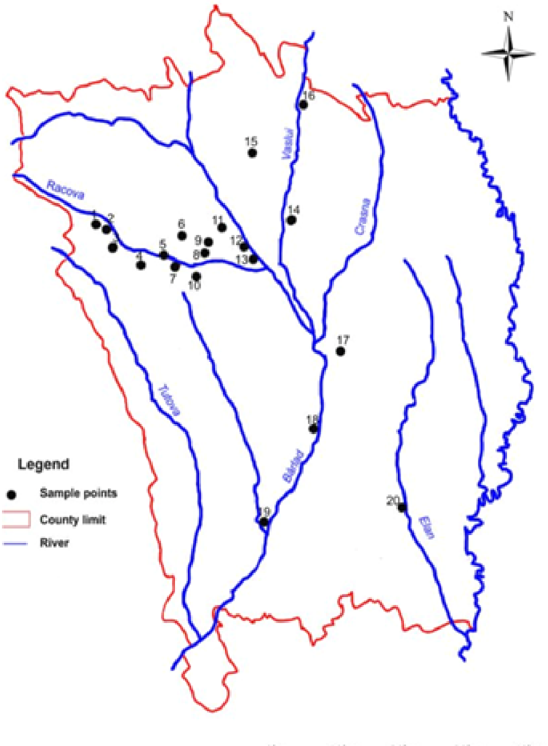

Fig. 2. Map of studied area showing sample locations Map with locations of the samples from studied area (Vaslui County, Romania): 1 - Silistea, 2 - Armasoaia, 3 - Blesca, 4 - Ivanesti, 5 - Harsoneni, 6 - Harsova, 7 - Poienesti, 8 - Laza, 9 - Sauca, 10 - Oprisita, 11 - Balteni, 12 - Brodoc, 13 - Rediu, 14 - Munteni de Sus, 15 - Feresti, 16 - Movila lui Burcel, 17 - Albesti, 18 - Sarbi, 19 - Simila, 20 - Giurcani

Physical parameters were measured on site: Total Dissolved Solids (TDS), electrical conductivity, salinity (SensION 5 Conductivity meter) and *p*H (SensION 1 portable pH meter). The analysis of nitrogen compounds (NH_4^+, NO_2^- and NO_3^- ions) was achieved, by spectrophotometric methods (microprocessor photometer MPM 1500). Ammonium was determined with Nessler reagent at 425 nm, while N-NO_2^- was determined by Griess-Saltzman method at 540 nm [31]. The procedure involves NO_2^- reaction with sulphanilamide to form a diazonium salt, which is subsequently combined with N-(1-naftil)-ethyldiamine, to form an azo-dye compound. Nitrate was reduced quantitatively to nitrite through a column with metallic Cd and it is analyzed following the same procedure as the nitrite ion. In this way, a content of total nitrogen in the form of nitrite ions (N_{tot} - NO_2^-) is determined. The concentration of nitrate ions is determined by subtracting the two measurements.

Results and discussions

Results of physical and chemical analyses

The analysis carried out on the field, has shown that the *p*H value for autumn season varies between 6.65 and 8.48 *p*H units (with an average value of 7.33), and from spring season varies between 6.66 and 8.60 (with an average value of 7.67). Significant difference in acidity of water occurred during the period of research. The spring results indicate strong acidification of water samples. Groundwater *p*H is between 6.5 - 9.5 [14], any deviation from these values giving an indication of inorganic pollution.

The analyzed samples were either slightly acid, or slightly basic and did not overcome the parameters of Romanian law. The small value of the standard deviation, shows that the results range around the average values.

The electric conductivity of the analyzed samples varies between 2.67 $\mu S\cdot cm^{-1}$ and 1830 $\mu S\cdot cm^{-1}$, with an average value of 970.87 $\mu S\cdot cm^{-1}$ in autumn samples, and between 2.72 $\mu S\cdot cm^{-1}$ and 1784 $\mu S\cdot cm^{-1}$, with an average value of 1075.48$\mu S\cdot cm^{-1}$ in spring samples. Water conductivity represents an important indicator in assessing the mineralization degree of a sample because it allows the determination of the total content of dissolved salts. From this point of view, the majority of the analyzed samples contain large quantities of salts, with conductivity values of the groundwater above the average value of 200 $\mu S\cdot cm^{-1}$ [32]. The samples with conductivity lower than 500 $\mu S\cdot cm^{-1}$ were situated especially in sandstone formations. The dispersion degree of the samples around average value was very high, which shows a non-homogeneous chemical composition of the analyzed samples.

Another parameter of groundwater quality is salinity, which offer informations on the salts quantity in a sample. All groundwater contains salts, from less than tens of milligrams per liter to a few grams per liter [33]. Normally, there are higher concentrations of dissolved salts in groundwater than in surface water as a result of longer exposure of soluble materials in geological structures to the water layer. The salinity from autumn samples varies between 0.20 and 1.60 ‰ (with an average value of 0.72 ‰), while the salinity from spring samples varies between 0.50 and 1.60 ‰ (with an average value of 0.75‰). Increasing salinity resulting from the effects of irrigated agriculture is one of the oldest and most widespread forms of groundwater pollution [34].

The notion of total dissolved solids (TDS) refers to all substances diluted in water (organic compounds, anorganic compounds and suspended materials) and is expressed in milligrams per liter [34]. The BIS [35] specifies a desirable total dissolved solids limit of 500 mg . L^{-1} and study area shows almost all samples were exceeding permissible limit (fig. 3). The TDS value for the analyzed samples varies between 245 $mg\cdot L^{-1}$ and 1579 $mg\cdot L^{-1}$, with an average value of 716 $mg\cdot L^{-1}$ in autumn samples, and between 452 $mg\cdot L^{-1}$ and 1603 $mg\cdot L^{-1}$, with an average value of 748.8 $mg\cdot L^{-1}$ in spring samples.

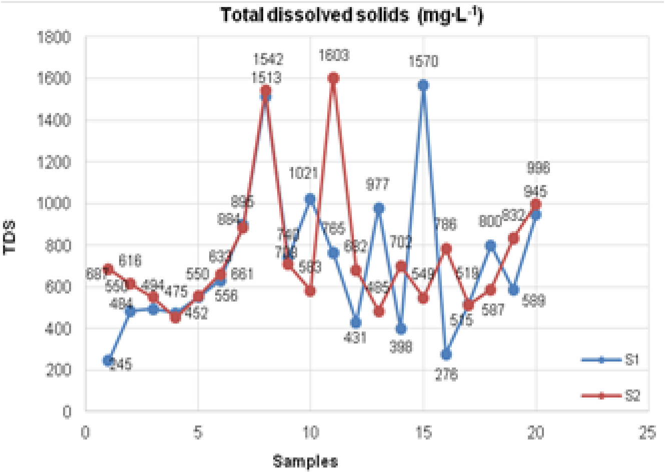

Fig. 3. Total dissolved solids values from study area (mg’ . L^{-1})

Results of nitrogen mineral compounds

The results of the present study are shown in table 2, which provides a comprehensive picture of the chemical characteristics of the water samples under analysis. The contamination of groundwater with nitrogen mineral compounds can be local (punctual sources) or regional (diffuse sources) and in the analysed area, agriculture and rural settlements represent potential sources. In groundwater, nitrogen is present in various forms (nitrite ion, nitrate ion, ammonium ion, nitrogen oxide, ammonia, gaseous nitrogen) and in various oxidation forms. Gaseous forms are relatively soluble in water and are not reactive, but ionic forms take part in the hydro-geo-chemical cycle of the nitrogen, and presents scientific interest. The form of maximum stability is represented by the nitrate ion, NO_3. In natural environments, the dissolved oxygen is consumed rapidly with the oxidation of the reduced forms, while lack of oxygen favours the reduction of the oxidized nitrogen forms. Also, bacteria activity is strongly involved in transitions between various oxidation states and the transportation mechanism of nitrogen compounds in groundwater is often complex [36].

The concentrations values of ammonium ions, NH_4^+, show an obvious variability of content between the two sets of measurements. For autumn samples values between 0.633 and 16.506 $mg\cdot L^{-1}$ (with an average value of 3.30 ± 3.76 $mg\cdot L^{-1}$) were registered, and for spring samples values between 1.61-10.90 $mg\cdot L^{-1}$ (with an average value of 2.539 ± 3.115 $mg\cdot L^{-1}$) were registered. If these values are measured against the limit values imposed by Romanian law (MAL = 0.50 $mg\cdot L^{-1}$), we notice that all

Table 1

PHYSICAL AND CHEMICAL ANALYSES

	pH		Electric conductivity ($\mu S\cdot cm^{-1}$)		Salinity (‰)		TDS ($mg\cdot L^{-1}$)	
	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2
Minimum	6.65	6.66	2.67	2.72	0.20	0.50	245	452
Average	7.33	7.67	970.87	1075.48	0.72	0.75	716	748.8
Maximum	8.48	8.60	1830	1784	1.60	1.60	1570	1603
SD	0.46	0.49	515.67	439.02	0.36	0.31	360.45	313.44

Sample	Pollution source	NO_2^- (mg·L^{-1})		NO_3^- (mg·L^{-1})		NH_4^+ (mg·L^{-1})	
		S1	*S2*	*S1*	*S2*	*S1*	*S2*
Simila	infield	0.34	2.58	5.59	4.02	0.70	5.48
Albesti	infield	0.41	3.23	6.54	5.08	1.41	2.05
Laza	livestock farms	1.25	18.52	1.25	23.82	0.63	1.62
Rediu	garbage dump	0.09	2.61	0.09	4.38	1.84	1.74
Silistea	livestock farms	0.09	2.46	0.09	4.46	16.51	5.59
Armasoaia	infield	0.56	6.62	34.50	10.08	3.26	1.86
Blesca	infield	0.18	2.64	0.19	4.12	1.87	2.06
Harsoveni	infield	0.34	3.42	0.75	5.52	8.91	8.27
Feresti	livestock farms	6.84	2.49	17.68	4.04	2.55	1.84
Brodoc	infield	0.75	2.49	16.97	3.96	3.56	1.75
Movila B.	infield	0.06	4.32	2.28	6.79	2.07	10.90
Sarbi	infield	8.03	2.52	27.66	4.01	1.87	1.99
Harsova	livestock farms	0.06	2.64	21.78	4.35	6.15	1.70
Giurcani	infield	0.62	2.70	1.640	6.77	0.70	1.61
Sauca	infiled	0.59	2.58	33.61	3.95	6	1.92
Balteni	garbage dump	0.31	2.64	3.90	4.20	1.34	1.99
Ivanesti	livestock farms	0.09	2.55	3.73	4.13	1.34	1.61
Munteni	livestock farms	1.93	2.89	4.38	4.65	2.58	1.86
Oprisita	garbage dump	0.62	2.64	2.03	6.68	1.18	3.01
Poienesti	garbage dump	1.09	3.11	23.55	4.82	1.44	3.44

Table 2
DISTRIBUTION OF CONCENTRATIONS OF NITROGEN MINERAL COMPOUNDS

content identified in the analysed area are well over the allowed limit; this can be explained if we consider that the analysed perimeter belongs to a rural area, where agriculture and use of chemical fertilizers are the main activity of the population. The use of boxplot diagram (Fig. 4a) which describes the ammonium concentrations shows a variable distribution of contents around the median value. In both sets of values, the median is closer to 1st quartile, which means that small concentrations values are predominant rather than large concentrations values. The diagram has shown two outliers values in autumn season and four outlier's values in spring season, respectively.

Contents of nitrite ions vary in large amounts for both autumn samples (between 0.06-8.03 mg·L^{-1}, with an average value of 1.21 ± 2.186 mg·L^{-1}) and spring samples (between 2.46-18.52 mg·L^{-1}, with an average value of 3.78 ± 3.599 mg·L^{-1}). It is important to notice that among autumn samples just eight exceed (more or less) the limit values of Romanian law (MAL = 0.50 mg·L^{-1}), while for spring samples all the values exceed this limit. The presence of a higher content of nitrite ion in ***S2*** samples indicates the presence of reducing conditions in the groundwater at the samples collected in May 2014, compared with the ones collected in December 2013. The boxplot type diagram used to describe the concentration value distribution indicates an asymmetrical distribution of these values around the median (fig. 4b). If for autumn samples the median is symmetrical to the two quartiles, for the values obtained in spring samples the median is close to the 1st quartile, that means low values are predominant and situations with big values are fewer. The diagram underlines for both seasons, three outlier concentration values each.

In the analysed samples the nitrate content varies in very large amounts for both seasons, without exceeding the imposed limit values by Romanian law (MAL = 0.50 mg·L^{-1}). Thus, the autumn samples have contents between 0.09 and 34.50 mg·L^{-1}, with an average value of 10.413 ± 11.884 mg·L^{-1}, and the spring samples have contents varying between 3.95 and 23.82 mg·L^{-1}, with an average value of 5.99 ± 4.46 mg·L^{-1}. The suboxic conditions of the groundwater of Vaslui County, Romania are underlined by the low values of nitrate concentrations. The boxplot type diagram used to study nitrate concentrations shows a variable distribution of the analysed samples, where small values are preponderant (fig. 4c). The diagram also shows only two outliers values.

In rural areas the contribution of nitrogen compounds to the pollution of groundwater is caused by anthropogenic activities (especially agriculture), exceeding the contribution caused by industrial activity. Excessive use of chemical fertilizers and/or synthetic fertilizers determines a deterioration of the quality of groundwater. Nitrification/denitrification processes of groundwater are not enough to eliminate nitrates, which reach the low depth aquifers in vegetal soil. These water layers are more sensitive to contamination, ensuring a significant contribution to the nitrite-nitrate content in surface waters [37]. Seasonal variations of the chemistry of groundwater are minor and are directly linked to the clay layer the water goes through [38]. Regarding the analysed samples, water taken from Rediu and Silistea, located on clay formations, presents

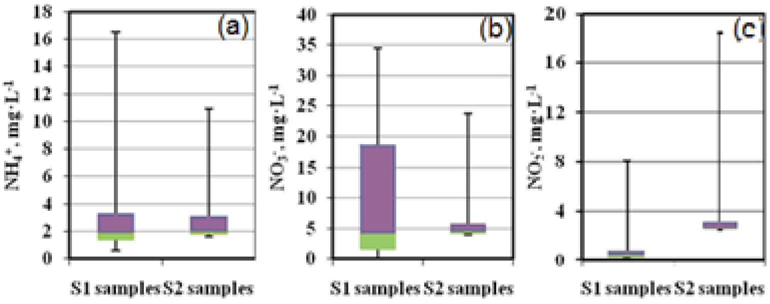

Fig. 4. Boxplot diagram for (a) ammonium ions, (b) nitrate ions, (c) nitrite ions

low concentrations of nitrates (0.09 $mg{\cdot}L^{-1}$), while water from Armasoaia, located on sandstone formations, presents high concentrations of nitrates ($NO_3^- = 34.50$ $mg{\cdot}L^{-1}$). The concentrations of nitrogen species are relatively stable for both seasons.

The relationship between nitrogen compounds in the analysed area was investigated in terms of the relative concentrations of three chemical species by using ternary diagrams NO_2^- - NO_3^- - NH_4^+ (fig. 5). The ternary-type diagram for both sets of data shows that nitrate ions are dominant over the other two ions and only four samples have a large content of ammonium ions. These samples belong to both sets of data and are exactly the samples taken from garbage dump sites. The samples with predominant nitrate ion show a good water oxygenation, because NO_3^- ion is the most stable form of nitrogen species, while samples with high ammonium ion (NH_4^+) or nitrite ion (NO_2^-) content are an indicator of reducing environments or recent pollution [39]. In our study, we noticed that for autumn season only 10 samples exceed the nitrite and ammonium contents recommended by Romanian laws.

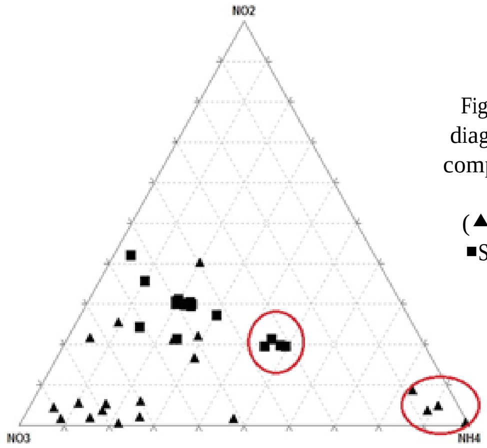

Fig. 5. Ternary diagram with the composition of all samples (▲S1 samples, ■S2 samples)

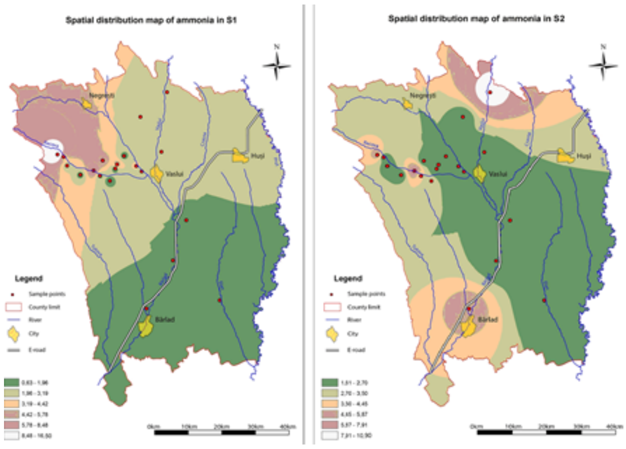

Fig. 6. Distribution maps of ammonium ions (mg . L^{-1})

Using ArcGIS 10.1 software, the vulnerability maps and the nitrogen concentration maps were realized, for the analyzed area of Vaslui County. The circles represented on the map indicate the location of monitored areas in the present study. For autumn season, ammonium ion concentrations in the northern part are higher (concentration interval between 4.42 and 8.48 $mg{\cdot}L^{-1}$) than concentrations in the southern part (concentration interval between 0.63 and 1.96 $mg{\cdot}L^{-1}$) of the analysed area (fig. 6). Higher values highlight the organic pollution of water sources, in most rural villages missing any sewage systemm, positioning latrines higher than the fountains place.

The highest concentration of ammonium ions was in Silistea (16.51 $mg{\cdot}L^{-1}$), in the western part of the analysed area. On the distribution map of ammonium ion for spring samples, we notice that low concentration values are predominant, rather than high concentration values. The sample located in the northern point of the analysed area (Movila lui Burcel) has the highest concentration of ammonium ions (10.90 $mg{\cdot}L^{-1}$). In this area the main source of ammonia in the atmosphere is agriculture. In surface waters appear large quantities of ammonia through degradation of protein and organic materials from waste plant and animal contained in the soil.

The distribution maps for nitrite ions are characterised by concentration values exceeding the norms allowed by Romanian law. Taking into account the fact that the samples of the study were mainly collected in areas close to agricultural lands, the presence of relatively high nitrite ions content proves that either chemical fertilizer are used in the area or there is no control of the waste disposal from the animal farms. Thus, for autumn samples (fig. 7) in the north-western part of the analysed area, low concentration values (0.06-0.84 $mg{\cdot}L^{-1}$) are predominant, while high values (much higher than MAL) are only punctual in Feresti (6.84 $mg{\cdot}L^{-1}$) and Sarbi (8.03 $mg{\cdot}L^{-1}$), because of intensive use of fertilizers for the cultivation of autumn wheat. The spring samples show concentration values slightly higher than autumn samples and their distribution shows that in the south-eastern part of the studied area, there are low concentration values (2.46-3.43 $mg{\cdot}L^{-1}$). We need to notice that in Laza, there was the highest concentration value for nitrite ions (18.52 $mg{\cdot}L^{-1}$), as well as nitrate ions, which make us to believe that the analysed samples are improper for domestic use. These values are high in this season because the area is an agricultural centre where subsistence farming is practiced extensively.

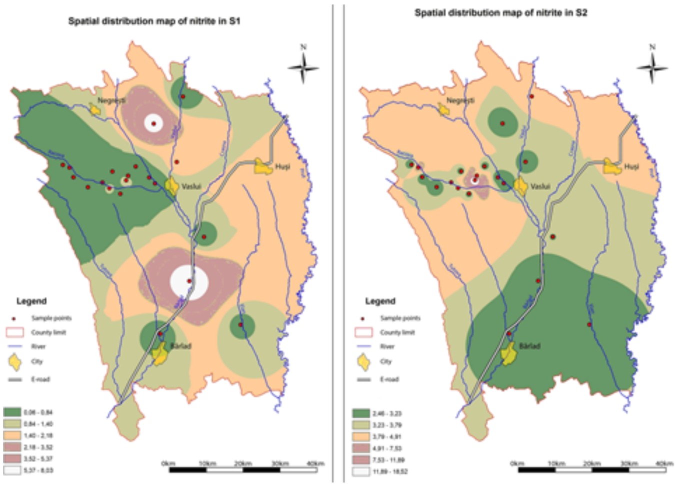

Fig. 7. Distribution maps of nitrite ion (mg . L^{-1})

The spatial distribution maps for nitrate ions, show small differences of concentrations between autumn and spring seasons, with slight preponderance of higher concentrations for autumn samples (fig. 8). In the northern and central part of Vaslui County, landscape is predominantly hilly and agricultural activities are practiced mainly, from uphill to downhill. Registered precipitations in these hilly areas wash agricultural lands more easily, with a high content of nitrate ions which can go into groundwater. Thus, we can notice seasonal modifications of nitrate concentrations, which led to the increase of the registered values in autumn samples and their decrease in spring samples.

As far as nitrate ions concentrations are concerned, spatial distribution maps show a heterogeneous distribution

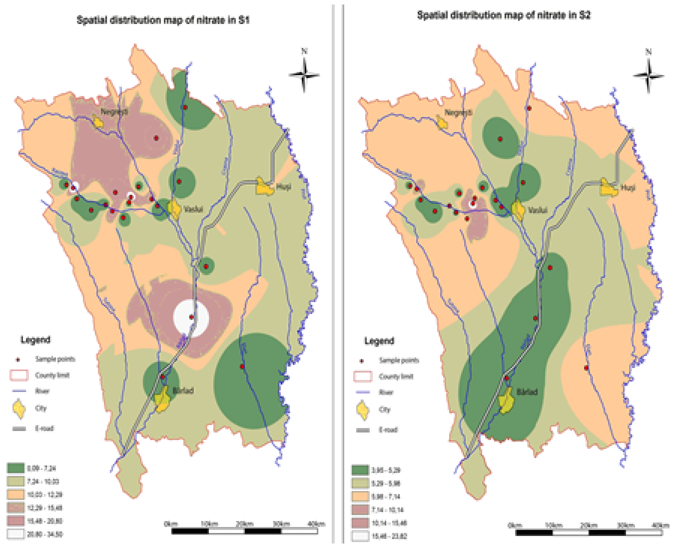

Fig. 8. Distribution maps of nitrate ion (mg . L^{-1})

content values for the two sets of samples. Thus, for autumn season (fig. 8) we notice a predominance of low (0-7.24 mg·L^{-1}) and medium (12.29-15.48 mg·L^{-1}) concentrations in the north-western and south-eastern parts of the studied area. High nitrate ion concentrations are registered in some isolated locations, that is in Armasoaia (34.50 mg·L^{-1}), Sauca (33.61 mg·L^{-1}) and Sarbi (26.76 mg·L^{-1}). In spring season, the samples show the same preponderance of low (3.96-5.29 mg·L^{-1}) and medium (7.14-10.14 mg·L^{-1}) values on the entire studied area. In this situation, the maximum registered value was in Laza (23.82 mg·L^{-1}) because occurs sewage overflow from the chicken farm Laza.

Conclusions

Located in the eastern part of Romania, on the middle course of Barlad River, Vaslui County is characterized by a non-homogeneous composition of groundwater. Nitrite and nitrate ion concentrations vary largely, but do not exceed the limits imposed by Romanian law, 50 mg·L^{-1} for nitrate, and 0.5 mg·L^{-1} for nitrite. The danger of groundwater consumption with nitrite and nitrate content is limited, taking into account the medical cases.

The analysis of nitrogen compounds contents has highlighted a series of conclusions:

- the studies samples were either lightly acid or lightly base and are within the limits of the quality parameters recommended by Romanian law. Most of the analysed samples contain high salt quantities, with conductivity levels over the average values of the underground waters of 200 ìS˝cm^{-1} in sandstone formations. The salinity and the total of dissolved solids for the two series of samples are within normal limits for the studied area.

- bmmonium ion concentrations, NH_4^+, show an obvious content variability between the two sets of measurements. We notice that all contents identified in the studied area exceed by far the limit recommended by Romanian law; this is normal because the analysed area belongs to a rural area where agriculture and the use of chemical fertilizers are the main occupation of the population. Nitrite ion concentrations vary to a large extent for both seasons. Numerous samples which exceed the values recommended by Romanian law have been identified. In the analysed samples the nitrate content varies to a large extent for autumn and spring seasons, without exceeding the values recommended by Romanian law. The suboxic conditions of the groundwater of Vaslui County, Romania are underlined by the low values of nitrate concentrations. The presence of a higher content of nitrite and ammonium ions indicates the presence of reducing conditions in the groundwater at the samples collected in May 2014, compared with the ones collected in December 2013.

- the relationship between nitrogen compounds in the analysed area was investigated in terms of the relative concentrations of three chemical species by using ternary diagrams. For both seasons, it was underlined that the nitrate ions dominate the other species, but also four samples situated close to the garbage dumps, have a large content of ammonium ions.

- the spatial distribution of ammonium ions from autumn samples show that in the northern part concentrations are higher than the concentrations in the southern part of the studied area, while from spring samples we noticed that low values are predominant, rather than high concentration values. For nitrite ions distribution maps are characterised by concentration values which exceed the norms established by the Romanian law. Thus, in autumn samples low concentration values are predominant in the north-western part of the analysed area, while high values appear only punctual. In spring season, samples show values with slightly higher concentrations than in autumn season, and their distribution shows that low concentration values are present in the south-eastern part. For nitrate ions there are small differences in concentrations between autumn and spring samples, with preponderance of higher concentrations for autumn samples.

References

1.PARDO-IGÚZQUIZA, E., CHICA-OLM, M., LUQUE-ESPINAR, J.A., RODRÍGUEZ-GALIANO, V., Science of the Total Environment, **532**, 2015, p. 162.

2.VASILACHE, V., CRETU, M.A., PASCU, L.F., RISCA, M., CIORNEA, E., MAXIM, C., SANDU, I.G., CIOBANU, C.I., International Journal of Conservation Science, **6** no. 1, 2015, p. 93.

3.ROMANESCU, G., ZAHARIA, C., SANDU, A.V., JURAVLE, D.T., International Journal of Conservation Science, **6** no. 4, 2015, p. 729.

4.ROMANESCU, G., COJOC, M.C., SANDU, I.G., TIRNOVAN, A, DASCALITA, D., SANDU, I., Rev.Chim (Bucharest), **66,** no 6, 2015, p. 855.

5.ADOPO, K.L., N'GUESSAN, M.Y., SANDU, A.V., ROMANESCU, G., SANDU, I.G., International Journal of Conservation Science, **7** no 2, 2016, p. 567.

6.ROMANESCU, G., IOSUB, M, SANDU, I., MINEA, I., ENEA, A, DASCALITA, D., HAPCIUC, O.E., Rev.Chim (Bucharest), **67,** no 1, 2016, p. 42.

7.ADDISCOTT, T.M., Nitrate, Agriculture Anthe Environment, Wallingford, Oxfordshire, UK, 2005, p. 279.

8.KOUAMÉ, I.K., KOUASSI, L.K., DIBI, B., ADOU, K.M., RASCANU, I.D., ROMANESCU, G., SAVANÉ, I., SANDU, I., Journal of Environmental Protection, **4**, 2013, p. 1441.

9.ROMANESCU, G., CRETU, M.A., SANDU, I.G., PAUN, E., SANDU, I., Rev. Chim. (Bucharest),**64**, no. 12, 2013, p. 1416.

10.PERRIN, A.S., PROBST, A.,. PROBST, J.L, Geochim Cosmochim Acta, **72,** no. 3, 2008, p. 105.

11.PELE, M., CAMPEANU, GH., ARTIMON, M., Roum. Biotechnol. Lett, **6**, no. 5, 2001, p. 437.

12.VOLKMER, B.G., ERNST, B., SIMON, J., KUEFER, R., BARTSCH, JR. G., BACH, D., GSCHWEND, J.E., Br. J. Urol. Int., **95**, 2005, p. 972.

13.WARD, M.H., DEKOK, T.M., LEVALLOIS, P., BRENDER, J., GULIS, G., NOLAN, B.T., Environ Health Perspect., **113**, 2005, p. 1607.

14.Law of Drinking Water no. 458/2002, - Monitorul Oficial al Romaniei nr. 552/29.VII.2002.

15.European Environment Agency, Europe's Environment: The Third Assessment, Copenhagen, 2003.

16.*** WHO, Guidelines for Drinking-water Quality. 3rd Ed, Vol. 1, Recommendations, Geneva, 2004, p. 417.

17.*** Australian Government, Australian Drinking Water Guidelines, Canberra, National Health and Medical Research Council, 2004.

18.*** Health Canada, Background Document for Canadian Drinking Water Guidelines: Nitrate/Nitrite, Ottawa, 1992.

19.*** Health Canada, Guidelines for Canadian Drinking Water Quality-Summary Table, Ottawa, Federal-Provincial-Territorial Committee on Drinking Water of the Federal Provincial-Territorial Committee on Health and the Environment, 2006.

20.*** Environmental Protection Agency, National Primary Drinking Water Standards (EPA-816/F-03-016), Washington DC, Office of Water, 2003.

21.IACOB, O., TUDOR, A., NEAMTU, A., CRISTEA, A., Well Water: Contamination by Nitrates and Methemoglobinemia (in Romanian), Carol Davila, Bucharest, 2012.

22.IONESI, L., Geology of platform units and North Dobrogea Orogen, (in romanian), Technical Press, Bucharest, Romania, 1994, p. 280.

23.MACAROVICI, N., Annals of Al.I. Cuza University, II. Natural Sciences, **4**, 1960, pp. 231.

24.URSACHI, L., CODREA, V.A., RATOI, B.G., VENCZEL, M., FARCAS, C., Scientific Bulletin of North University Center of Baia Mare, **30**, no. 1, 2016, p. 79.

25.CODREA, V.A., RATOI, B.G., URSACHI, L., SOLOMON, A., BRANZILA, M., Studies and Communication, Natural Sciences (Oltenia Museum Craiova), **29** no. 1, 2013, p. 19.

26.CODREA, V.A., URSACHI, L., RATOI, B.G., BRANZILA, M., Elanul, **163**, 2015, p. 1.

27.CODREA, V.A., RATOI, B.G., URSACHI, L., FARCAS, C., Studies and Communication. Natural Sciences (Oltenia Museum Craiova), 2016, p. 79.

28.ROMANESCU, G., PAUN, E., SANDU, I., JORA, I., PANAITESCU, E., MACHIDON, O., STOLERIU, C., Rev. Chim. (Bucharest), **65** no. 4, 2014, p. 401.

29.ROMANESCU, G., SANDU, I., STOLERIU, C., SANDU, I.G, Rev. Chim. (Bucharest), **63** no. 3, 2014, p. 344.

30.PETA, C., Barlad Valley-ecology and hydrology studies, PhD Thesis, Faculty of Geography, Bucharest University, Romania, 2007.

31.MANESCU, S., CUCU, M., DIACONESCU, M., Sanitary chemistrya of environmental (in Romanian), Medical Press, Bucharest, Romania, 1994, p. 353.

32.TRUFAS, V., TRUFAS, C., Hydrochemistry, (in Romanian), University Press, Bucharest, Romania, 1975.

33.PRICAJAN, A., Mineral and thermal waters from Romania, (in Romanian), Technical Press, Bucharest, Romania, 1972, p. 296.

34.MEYBECK, M., CHAPMAN, D., HELMER, R., Global Freshwater Quality: A First Assessment. Blackwell Reference, Oxford, 1989, p. 306.

35.*** Bureau of Indian Standards, New Delhi, Guidelines for Drinking-water Quality, 1991.

36.KLIMAS, A., PAUKSTYS, B., NGU Bull., **424**, 1993, p. 75.

37.STUART, M.E., GOODDY, D.C., BLOOMFIELD, J.P., WILLIAMS, A.A., Sci. Total Environ., **409**, 2011, p. 2859.

38.VYSTAVNA, Y., YAKOVLEV, V., DIADIN, D., VERGELES, Y., STOLBERG, F., Environ. Earth Sci., **74**, 2015, p. 585.

39.BUCCIANTI, A., NISI, B., MARTÍN-FERNÁNDEZ, J.A., PALAREA-ALBALADEJO, L., Journal of Geochemical Exploration, **141**, 2014, p. 78

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