

INTERPRETATION OF ISOTOPIC DATA FOR GROUNDWATERS IN THE OLĂNEȘTI AREA. COMPARISONS WITH OTHER CARPATHIAN ZONES

Delia Cristina Papp^{1*}, Laurențiu Asimopolos¹, Violeta Carolina Niculescu², Natalia-Silvia Asimopolos¹

¹Geological Institute of Romania, 1, Caransebeș Street, 012271 – Bucharest, Romania

²National Research and Development Institute for Cryogenics and Isotopic Technologies – ICSI Rm. Valcea, 4 Uzinei Street, P.O. Box Râureni 7, 240050, Rm. Valcea, Romania

Abstract:

The research activities consisted in the inventory of stable hydrogen isotopic and geochemical data for mineral and geothermal waters belonging to the Olănești resort in order to define their origin, genetic relationships and underground dynamics in the geological context of the Getic Depression. Comparative study with other Carpathian zones (i. e. East Carpathians, Apuseni Mountains, Pannonian Basin, Transylvanian Basin, Getic Depression, and External Flysch) has also been performed. Previous hydrogeological, hydrochemical and isotopic studies identified three components for the groundwaters in the Olănești area: deep formation waters, local infiltration waters (especially from the Olănești Valley), and waters from high altitudes. Formation waters from Olănești and from other resorts in the Getic Depression (Călimenești – Căciulata and Govora) display mean δD and TDS values similar to those of formation waters in the Balványos - Covasna area (East Carpathians), and also to the salt waters in the Transylvanian Basin. The major contribution of formation water to the genesis of mineral waters in the Getic Depression makes them extremely vulnerable to degradation over time because formation water is a „fossil” not renewable component.

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*Corresponding author: Delia Cristina Papp, E-mail: mail.deliapapp@gmail.com

1. INTRODUCTION

Groundwater is the largest supply of freshwater in the world. Therefore, the groundwater quantity and quality are of great importance for the economic development as groundwater is the most important resource for drinking water, irrigation, as well as for industrial uses. Groundwater is also a pillar to ecosystem health. Quality of the groundwater is linked to the presence of dissolved elements from geogenic (natural) origin altered by elements of anthropogenic origin.

Application of integrated stable hydrogen isotope and hydrogeochemical models to the groundwater systems provides important information on their sources, mixing phenomena and underground dynamics (e.g. Bojar et al., 2021a). Surface water systems (running water, lakes, wetlands, reservoirs) as well as the infiltration of local precipitation are possible sources of recharge to the groundwater system. In the underground, water belonging to the meteoric cycle can be mixed with water of different sources or origins of which fossil formation water is the most important component. Such mixing phenomena can be appropriately studied using the correlations between deuterium concentration and total salt content of the water (e.g. Gat, 1971; Blaga et al., 1975; Payne, 1981; Papp and Cociuba, 2011; Papp et al., 2017). For underground water, and for geothermal water in particular, water/rock interaction processes could affect their isotopic composition. For oxygen isotopes, the extent of exchange could be significant, depending on the relative proportions of oxygen in the water and in the rocks. In contrast, the initial hydrogen isotope composition of water is much less affected because the hydrogen content of rocks is generally too low to significantly affect the isotopic composition of underground water. Therefore, the use of hydrogen isotope composition (deuterium concentration) of water for the purpose of identifying the origin of the water is preferred to the use of oxygen.

The main objective of the present study is to link the isotopic composition of groundwaters to the geological settings and the hydrogeological processes in order to better account for the risk of groundwater degradation. The research activities consisted in the inventory of isotopic and geochemical data for mineral and geothermal waters belonging to the Olănești resort and carrying out a comparative study with other Carpathian zones (i. e. East Carpathians, Apuseni Mountains, Pannonian Basin, Transylvanian Basin, Getic Depression, and External Flysch).

2. GEOLOGICAL SETTING OF THE OLĂNEȘTI HYDROMINERAL DEPOSIT

From a geological point of view, the Olănești resort is located in the Getic Depression (Figure 1). In the Getic Depression, the hydromineral deposits genetically belong to the Eocene and Miocene formations. Mineral waters have a predominant sulphurous and chlorosodium character (Pricăjan, 1985). The occurrence of mineral waters allowed the development of several spas, of which the most important are those on the Olt Valley, respectively Căciulata, Călimănești, Olănești and Govora (Roanghes-Mureanu, 2012).

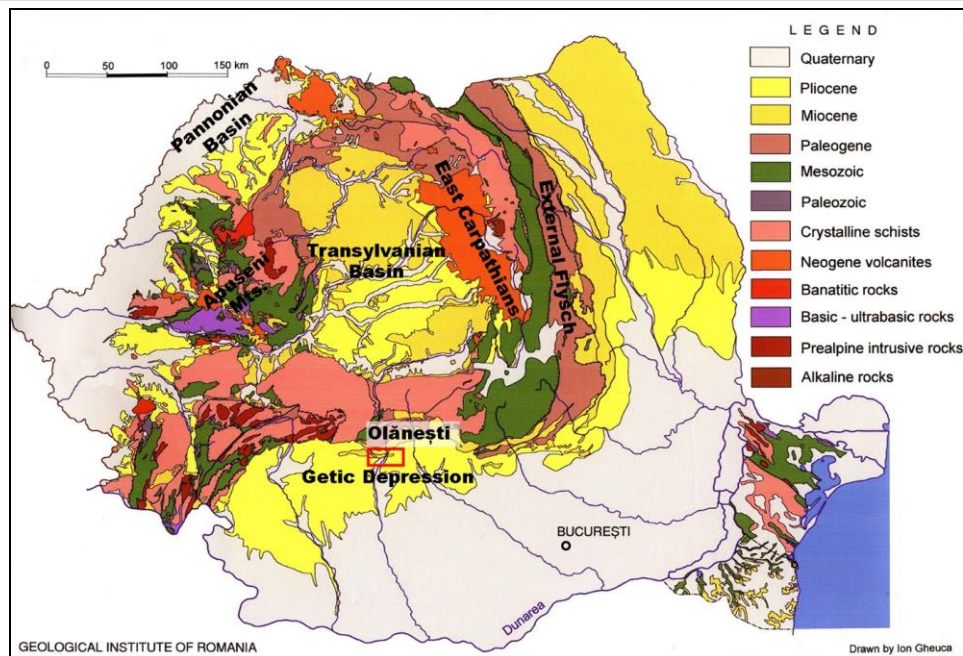


Figure 1. Geological sketch map of Romania showing the location of the study areas

The main features that define the hydrogeological conditions of the Getic Depression are (Pascu, 1981): the development of coarse detrital rocks in the Badenian - Villafranchian stratigraphic interval; moderate relief energy; the absence of eruptive formations; the absence of post-volcanic manifestations; a quiet tectonic framework, with anticlines and synclines in the northern-central area, and a monoclinial style in the rest of the depression; the existence of areas of neotectonic subsidence, which have led to the occurrence of hydrographic convergences: widespread of alluvial cone deposits; in some areas, where rivers flow on Pliocene sands or Căndești gravels, they lose part of their flows, and sometimes dry out completely; Pliocene deposits contain important reserves of groundwater under pressure; locally, the presence of evaporites determines high mineralization of groundwater; due to the presence of hydrocarbon deposits, associated waters with very high mineralization, as well as thermal waters occur.

The main types of hydrogeological structures in the Getic Depression are: (1) alluvial structures, including terraces and alluvial cone deposits; (2) hydro-structures, fed by the discharge of hydrocarbon structures and from the hydrographic network; (3) deep hydro-structures in Miocene - Pliocene granular formations (waters under pressure having an artesian character).

The Olănești hydromineral deposit is in the Olănești river basin (Figure 1), at the morphostructural contact between the Căpățâni Mountains and the sub-Carpathian hills of Oltenia (Olănești hills). It currently functions as one of the most important spas in the Getic sub-Carpathian area (Oprea, 2009). The area consists of monoclinial sedimentary formations of Upper Cretaceous, Eocene and Oligocene over the metamorphic formations of the Southern Carpathians. The mineral waters are accumulated in the Eocene and Oligocene conglomerates, as well as in the Senonian sandstones (Pricăjan, 1985). Groundwater circulation took place on the fault system, as well as on the stratification surfaces, and its ascent is favoured by the presence of gases, mainly methane. In the

Olănești area, the hydromineral deposit is exploited through over 30 springs and several drillings.

The main types of mineral waters are (Pricăjan, 1972): (1) sulphurous, bicarbonate, sulphated, sodium, calcium, magnesium waters with a total mineralization of 500 - 1000 mg/l and H₂S content between 0.1 and 9 mg/l; (2) sulphurous, chlorinated, bicarbonate, sodium waters with a total mineralization of 1300 mg/l; (3) sulphurous, chlorinated, brominated, iodinated, sodium, calcium, magnesium waters, found in most boreholes in the area, with a mineralization between 1500 and 3000 m/l and an H₂S content varying between 5 and 20 mg/l. The H₂S is considered of organic origin, resulting from the reduction of sulphates by specific anaerobic bacteria in the presence of hydrocarbons.

3. MATERIALS AND ANALYTICAL METHODS

Over 80 water sources comprising mineral springs, boreholes (wellhead water) and surface waters has been taken into consideration for the Olănești area. The database includes measurements of deuterium concentration (δD) and of total dissolved solids (TDS), as well as chemical analyses of Li, Na, K, Mg, Ca, and Sr. The analyses were performed by the National Research and Development Institute for Isotopic and Molecular Technologies, Cluj-Napoca (Blaga et al., 1975, 1979a, 1979b; Blaga & Florian, 1984).

For other Carpathian zones, the database that we used for comparisons comprises isotopic and chemical analyses, performed between 1970 and 2014, on a large number of springs, wellhead water, domestic wells, karst springs, cave water, mine waters, salt waters related to gas deposits, as well as surface running waters, lakes and precipitation. The database was created within the PN 09210306 project (Papp, 2014) and is accompanied by a detailed statistical analysis. The East Carpathians, Apuseni Mountains, Pannonian Basin, Transylvanian Basin, Getic Depression, and External Flysch are the main areas of provenance for the water samples.

All water sources have been periodically sampled over one or two years of observation. Deuterium concentration and total dissolved solids were measured both in the underground sources and in the surface sources, in order to include all water types that might interact. All isotopic data are expressed in conventional δD notation as the per mil deviation of D/H ratios with respect to the V-SMOW standard. The content of total dissolved solids was measured using a digital densimeter and is expressed as the density difference of sample water relative to standard distilled water, at 25°C. It is noted as TDS and expressed in units of mg/l. Major solutes within the groundwater samples (Li, Na, K, Mg, Ca, and Sr) were determined using absorption spectroscopy.

4. RESULTS AND DISCUSSION

4.1. Mineral and geothermal waters from Olănești

Hydrogeological, hydrochemical and isotopic studies in the Olănești area (Blaga et al., 1975, 1979a, 1979b; Blaga & Florian, 1984) showed that despite the large number of sources, the δD values vary between relatively narrow limits, between -57‰ and -75‰, for both underground and surface sources (Table 1). For surface water in the area, similar results have been obtained for the Olt Valley rivers (Popescu et al., 2011). In contrast, the TDS values vary significantly from one source to another. Values range from 40 mg/l in surface water and can reach extreme values of 13000 mg/l in some boreholes. Based on the

variation of the two parameters, three types of water have been distinguished: (1) surface waters with a low salt content and relatively high variability of deuterium concentration, (2) medium depth waters with a higher salt content, and (3) deep, highly mineralized waters with relatively high deuterium concentration.

Table 1. Mean values of δD , TDS and major solutes for different water sources from Olănești (data from Blaga et al., 1975, 1979a, 1979b; Blaga & Florian, 1984; Papp, 2014)

Source	δD ‰	TDS mg/l	Li mg/l	Na mg/l	K mg/l	Mg mg/l	Ca mg/l	Sr mg/l
Spring no. 3	-64.43	5861	0.86	2826	56.94	106.67	240.78	25.91
Spring no. 4	-62.82	6250	0.81	2659	53.94	102.56	236.44	25.39
Spring no. 5	-66.80	3997	0.50	2044	35.56	60.50	128.63	13.56
Spring no. 5a	-68.76	4481	0.53	2195	36.60	65.50	176.50	17.60
Spring no. 5b	-68.33	4500	0.50	1990	37.95	60.50	185.50	17.65
Spring no. 5c	-68.44	4322	0.51	2395	37.20	63.50	178.50	18.60
Spring no. 5d	-68.65	4051	0.50	2238	38.50	62.00	177.50	17.65
Spring no. 5e	-65.55	2522	0.45	1680	31.00	61.00	182.00	16.20
Spring no. 6	-62.34	6884						
Spring no. 7	-67.70	4349	0.45	1932	32.28	57.53	123.11	13.00
Spring no. 8	-68.11	2414	0.32	1452	23.46	42.20	86.56	8.76
Spring no. 8c	-72.61	1837						
Spring no. 8bis	-74.54	1663	0.12	800	8.50	9.30	15.00	0.84
Spring no. 9	-71.85	2538	0.16	949	11.96	16.23	26.78	2.53
Spring no. 10	-68.03	1239	0.14	717	10.98	28.28	48.33	2.75
Spring no. 11	-62.79	609		95	4.70	34.63	44.00	0.69
Spring no. 12	-64.90	643		229	4.35	16.94	41.88	0.33
Spring no. 13	-71.97	1518	0.10	720	8.50	8.58	15.33	1.05
Spring no. 14	-73.90	1690	0.27	781	9.23	9.25	97.00	7.09
Spring no. 15	-68.30	4989	0.55	2224	37.81	63.44	141.67	15.87
Spring no. 16	-69.12	4712	0.49	2189	39.09	58.00	134.00	14.11
Spring no. 17	-68.51	4283	0.45	1890	32.25	53.20	101.01	11.48
Spring no. 18	-68.22	4094	0.42	1766	30.54	55.12	115.40	11.18
Spring no. 19	-66.74	5062	0.63	2088	49.24	69.32	136.00	14.27
Spring no. 21	-64.09	1308	0.17	480	14.75	32.15	51.00	2.85
Spring no. 23	-64.82	2217	0.28	920	21.75	36.30	51.00	5.90
Spring no. 24	-63.03	509		100	3.80	28.80	11.00	0.52
Spring no. 25	-63.69	5389						
Spring no. 26	-64.99	2514						
Spring no. 27	-63.17	4423	0.63	2043	42.17	91.94	191.22	18.59
Spring no. 28	-62.10	7316						
Spring no. 29	-62.82	6192						
Spring no. 30	-67.07	3477	0.39	1645	29.25	45.80	89.50	10.05
Spring N1	-62.02	183						
Spring	-63.22	513						
Spring	-67.36	1289	0.16	673	8.50	18.30	31.50	1.91
Spring	-63.94	386		26	3.30	24.90	37.00	0.34
Spring	-69.62	1541						
Spring	-68.76	1805						
Spring	-68.12	1635						
Spring	-71.97	1565						
Spring	-62.08	1272	0.29	650	14.75	76.25	100.50	7.40
Spring	-64.91	112						
Spring	-58.49	187						

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Spring	-68.12	1116						
Spring	-58.49	483						
Spring	-55.84	560						
Borehole N1	-62.96	8084	1.18	3440	68.75	159.25	63.00	37.15
Borehole N2	-57.47	13072	1.82	5447	124.67	273.17	639.83	70.43
Borehole N3	-57.94	11533	1.51	4910	101.25	219.75	636.25	62.23
Borehole N4	-62.74	9353	1.26	4585	75.63	156.13	155.25	44.25
Borehole N5	-71.06	4563						
Borehole	-63.16	290		22	2.40	25.15	18.00	0.35
Drain	-62.62	488						
Tisa stream	-58.20	412						
Biser stream	-62.16	213						
Olănești upstream	-62.20	165						
Olănești downstr.	-63.24	88						
Cheia stream	-67.56	92						
Folea stream	-67.64	46						
Icoane stream	-59.40	164						
V. Lungă	-58.81	131						
Stream	-55.35	408						
Stream	-60.03	329						
Stream	-64.91	40						
Stream	-59.77	222						
Stream	-65.39	184						

Both surface waters and mineral waters show seasonal variations in δD values and TDS. For surface waters, seasonal variations of δD values are between the same limits for all studied sources, but the minimum and maximum sequences differ from one source to another. For running water, the δD values are at the maximum level in the summer - autumn months, due to the intense evaporation during the warm periods. The lowest values are found in the spring months when contribution of melted snow is significant. The highest TDS values appear in the autumn - winter months when the contribution of precipitation and infiltration water is low. During the spring months (March - April) the infiltration of surface water intensifies due to snow melt runoff, and as a result there is a dilution of groundwater.

For the Olănești area, it was possible to count for the effect of the earthquake from 1978 on the groundwater system (Blaga et al., 1979b). Higher flows of mineral springs were observed after the earthquake, probably due to the opening of some fractures. For some sources (e. g. Spring no. 8, sulphurous spring Comanca), both δD and TDS values increased significantly after the earthquake, which can be explained by the opening of paths for the migration of deep water to the surface.

Regarding the seasonal variations in the main cations (Li, Na, K, Ca, Mg, Sr), they follow the seasonal variations of the total mineralization, with minimums in the spring months and maximums in the winter months.

Within the Olănești hydromineral deposit, positive correlations were obtained between the δD values, TDS and main cations (mean values) (Table 2), which suggests similar solubilization and transport mechanisms for all water sources. Li, Na, K, Mg, K show significant positive correlations with the δD values (correlation coefficient, r , varying between 0.80 and 0.89) and the TDS values (r varying between 0.97 and 0.99). Ca also shows positive correlations with δD and TDS, but less significant ($r = 0.78$ and $r = 0.88$, respectively). Positive correlation coefficients (r varying between 0.85 to 0.99) were

obtained for Li, Na, K, Mg, Ca and Sr. All these results suggest that mineralization occurred predominantly through psamitic and pelitic rocks. Due to its lower ionic potential, K is easily absorbed into clays, and as a result the waters contain more Na than K.

Tabel 2. The correlation matrix between the δD , TDS and main cations for several groundwater sources in the Ol ăne ști area

	Mean	Std. dev.	δD	TDS	Li	Na	K	Mg	Ca	Sr
δD (‰)	-66.49	4.75	1.00	0.81	0.84	0.80	0.85	0.89	0.78	0.84
TDS (mg/l)	4928.45	3584.12	0.81	1.00	0.99	0.99	0.99	0.97	0.88	0.98
Li (mg/l)	0.63	0.51	0.84	0.99	1.00	0.98	0.99	0.99	0.89	0.99
Na (mg/l)	2241.33	1512.05	0.80	0.99	0.98	1.00	0.98	0.96	0.85	0.98
K (mg/l)	42.39	33.84	0.85	0.99	0.99	0.98	1.00	0.99	0.91	0.99
Mg (mg/l)	82.88	76.59	0.89	0.97	0.99	0.96	0.99	1.00	0.90	0.99
Ca (mg/l)	182.34	186.33	0.78	0.88	0.89	0.85	0.91	0.90	1.00	0.92
Sr (mg/l)	20.74	20.85	0.84	0.98	0.99	0.98	0.99	0.99	0.92	1.00

4.2. Comparison with groundwaters from other Carpathian zones

In all studied areas (East Carpathians, Apuseni Mountains, Pannonian Basin, Transylvanian Basin, Getic Depression, and External flysch), the δD values of mineral and geothermal waters, of salt waters, and of mine waters vary between limits similar to those of surface waters (Table 3), which shows that groundwater belongs mostly to the meteoric cycle regardless of the type of deposits in which they are located.

Tabel 3. Distribution of δD values and total dissolved solids (TDS) of groundwater in the area of Getic Depression (Ol ăne ști, C ălim ăne ști-Căciulata, Govora) compared to groundwater in other Carpathian areas ([data from Papp, 2014](#))

	Mean value	Min value	Max value
Getic Depression			
(Ol ăne ști, C ălim ăne ști-Căciulata, Govora)			
<i>Groundwater</i>			
δD (‰ V-SMOW)	-66.33	-78.3	-56.7
TDS (mg/l)	3261.8	57.3	13672.8
<i>Formation water</i>			
δD (‰ V-SMOW)	-33.5	-57.9	-8.7
TDS (mg/l)	26906.9	11533.5	58992.9
<i>Surface water</i>			
δD (‰ V-SMOW)	-62.5	-73.6	-55.3
TDS (mg/l)	333.3	40.0	1387.4
Harghita - Covasna			
<i>Groundwater</i>			
δD (‰ V-SMOW)	-74.9	-76.8	-72.6
TDS (mg/l)	1778.4	1102.0	24295
<i>Formation water</i>			
δD (‰ V-SMOW)	-38.9	-44.8	-32.9
TDS (mg/l)	23026.5	21758.0	24295.0
<i>Surface water</i>			
δD (‰ V-SMOW)	-74.9	-77.1	-73.6
TDS (mg/l)	330.7	295.0	392.0

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Sângeorz Băi			
<i>Groundwater</i>			
δD (‰ V-SMOW)	-77.3	-79.1	-51.1
TDS (mg/l)	2373.5	286.9	6030.8
<i>Formation water</i>			
δD (‰ V-SMOW)	-43.5		
TDS (mg/l)	8384.0		
<i>Surface water</i>			
δD (‰ V-SMOW)	-71.8	-78.0	-62.1
TDS (mg/l)	156.4	81.3	308.9
Pădurea Craiului			
<i>Groundwater</i>			
δD (‰ V-SMOW)	-71.9	-74.7	-69.3
TDS (mg/l)	261.1	48.9	366.2
<i>Surface water</i>			
δD (‰ V-SMOW)	-72.7	-76.5	-66.8
TDS (mg/l)	151.0	47.6	665.0
Pannonian Basin (Băile Felix - Oradea)			
<i>Groundwater</i>			
δD (‰ V-SMOW)	-67.5	-76.1	-33.5
TDS (mg/l)	1076.9	348.0	9248.0
<i>Surface water</i>			
δD (‰ V-SMOW)	-53.2	-55.6	-50.7
TDS (mg/l)	372.8	343.8	401.9
<i>Formation water</i>			
δD (‰ V-SMOW)	-35.4	-37.3	-33.5
TDS (mg/l)	7205.0	5162.0	9248.0
Pannonian Basin (Oradea – Carei – Satu-Mare)			
<i>Groundwater</i>			
δD (‰ V-SMOW)	-60.5	-77.6	-50.6
TDS (mg/l)	3148.7	383.3	7239.7
<i>Surface water</i>			
δD (‰ V-SMOW)	-51.7	-64.5	-39.0
TDS (mg/l)	439.6	297.5	581.7
Slănic Moldova (External flysch)			
<i>Groundwater</i>			
δD (‰ V-SMOW)	-64.6	-77.5	-53.1
TDS (mg/l)	6873.8	75.0	16895.6
<i>Surface water</i>			
δD (‰ V-SMOW)	-71.8	-75.4	-69.2
TDS (mg/l)	1248.9	113.6	8372.0
Transylvanian Basin (Bazna)			
<i>Formation water</i>			
	-8.7	-15.7	+0.9
δD (‰ V-SMOW)	39800.3	36846.0	42087.0
TDS (mg/l)			
<i>Salt water</i>			
δD (‰ V-SMOW)	-41.3	-45.8	-38.0
TDS (mg/l)	42347.0	25149.0	49702.0

<i>Surface water</i>			
δD (‰ V-SMOW)	-62.5	-68.1	-45.7
TDS (mg/l)	2482.4	589.0	11083.0
Zlatna (Apuseni Mts.)			
<i>Groundwater</i>			
δD (‰ V-SMOW)	-67.4	-70.1	-63.5
TDS (mg/l)	210.5	60.0	419
<i>Surface water</i>			
δD (‰ V-SMOW)	-70.2	-72.8	-67.5
TDS (mg/l)	247.5	39.0	985.0
<i>Mine water</i>			
δD (‰ V-SMOW)	-72.4	-76.1	-69.5
TDS (mg/l)	1358.7	81.0	3326.0
Baia-Borșa – Rodna (East Carpathians)			
<i>Mine water</i>			
δD (‰ V-SMOW)	-79.1	-84.8	-73.4
TDS (mg/l)	391.2	121.4	661.0
<i>Surface water</i>			
δD (‰ V-SMOW)	-84.9	-93.3	-76.5
TDS (mg/l)	180.7	25.0	155.7
Cacova Ierii, Băița-Bihor (Apuseni Mts.)			
<i>Mine water</i>			
δD (‰ V-SMOW)	-73.3	-78.7	-67.8
TDS (mg/l)	734.0	115.00	1353.00
<i>Surface water</i>			
δD (‰ V-SMOW)	-78.4	-81.3	-75.4
TDS (mg/l)	126.8	31.00	222.5
Upper Olt river catchment			
δD (‰ V-SMOW)	-71.1	-79.0	-64.6
TDS (mg/l)	166.9	43.5	400.0
Upper and middle Mureș catchment			
δD (‰ V-SMOW)	-66.3	-79.0	-55.3
TDS (mg/l)	106.9	38.8	1122.8
Upper Someșul Mare river catchment			
δD (‰ V-SMOW)	-74.1	-80.0	-69.4
TDS (mg/l)	203.2	92.8	576.6
Criș rivers catchment			
δD (‰ V-SMOW)	-66.1	-70.7	-55.3
TDS (mg/l)	115.3	35.6	402.5

The variation plot between the mean δD and TDS values for groundwater and surface water in different Carpathian areas (Figure 2) clearly shows the separation of fossil formation water (δD between -43.5‰ and -8.7‰ and TDS between 7205mg/l and 42347mg/l) from the rest of the groundwater and surface water belonging to the present meteoric cycle which are characterized by δD values between -85‰ and -51.7‰, and TDS values between 107mg/l and 6874mg/l.

INTERPRETATION OF ISOTOPIC DATA FOR GROUNDWATERS IN THE OLĂNEȘTI AREA. COMPARISONS WITH OTHER CARPATHIAN ZONES

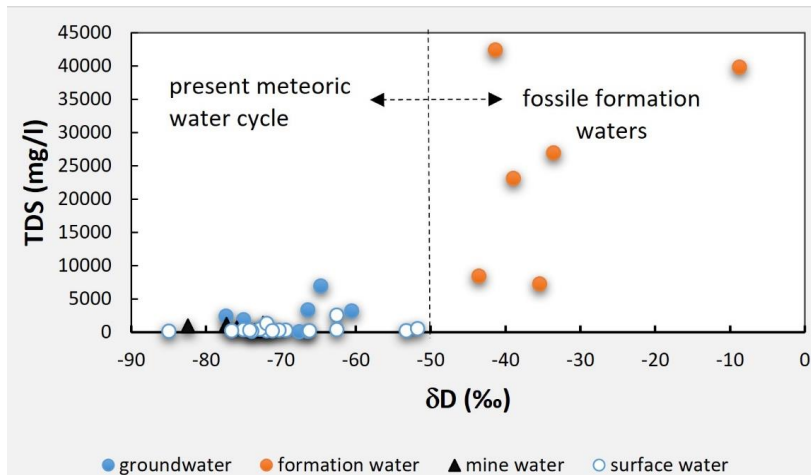


Figure 2. Variation plot of the mean δD (‰) and TDS (mg/l) values of groundwater, fossil water, mine water and surface water in different Carpathian zones

The mean values of δD and TDS of groundwaters in the Olănești area (Getic Depression) as compared to groundwaters belonging to the present meteoric cycle in different Carpathian zones are plotted in Figure 3 (data from Papp, 2014). It shows that the groundwaters in the East Carpathians (Harghita - Covasna and Sângeorz Băi areas) are characterized by the lowest δD values (between $-77‰$ and $-75‰$) as compared to other Carpathian areas, suggesting that these waters originate mainly from infiltrations at high altitudes. Their TDS values vary between 1778 mg/l and 2374 mg/l. Groundwaters in the Pădurea Craiului Mountains and those in the Pannonian Basin (Băile-Felix Oradea) are characterized by slightly higher δD values (between $-72‰$ and $-67‰$) but have much lower salinities (<1700 mg/l). Groundwaters in the deposits of the Pannonian Basin (Oradea - Satu Mare), the Getic Depression (Olănești, Călimănești - Căciulata, Govora), and the External Flysch (Slănic Moldova) show δD values typical for waters from the meteoric cycle (between $-66‰$ and $-60‰$), but their TDS values are much higher (> 3100 mg/l). The waters from the External Flysch display the highest TDS mean values (> 7000 mg/l) due to the presence of salt deposits.

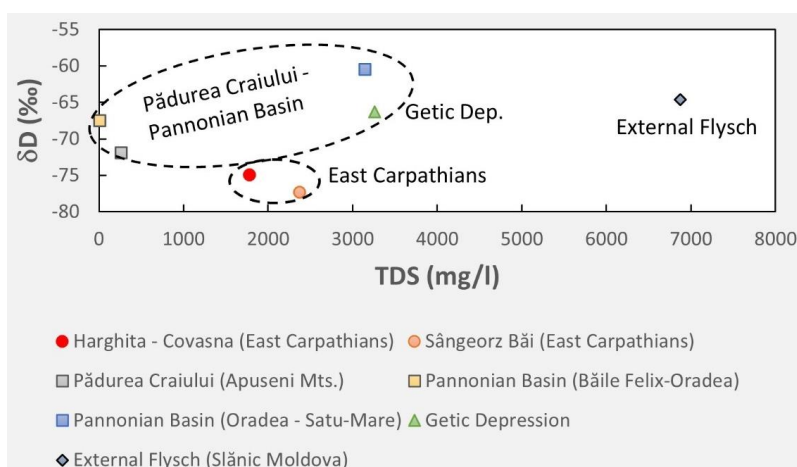


Figure 3. Variation plot of the mean δD (‰) and TDS (mg/l) values of

groundwater belonging to the present meteoric cycle in different Carpathian zones

Fossil formation waters differ in terms of isotopic composition and total dissolved solids from one area to another (Figure 4). The formation waters from Bazna (Transylvanian Basin) display the highest δD values and of total dissolved solids ($\delta D = -8.7\text{‰}$ and $TDS = 39800\text{ mg/l}$). These values are typical values for formation waters, unaltered or altered in a very small proportion by mixing with surface waters. The salt waters from the Transylvanian Basin, whose salinity comes from the dissolution of salt deposits, display TDS values similar to those from Bazna, but their δD values are lower, falling within the variation range of other formation waters in the the Getic Depression, East Carpathians (Harghita - Covasna, Sângeorz Băi), and the Pannonian Basin ($\delta D = -43.5\text{‰} \div -33.5\text{‰}$).

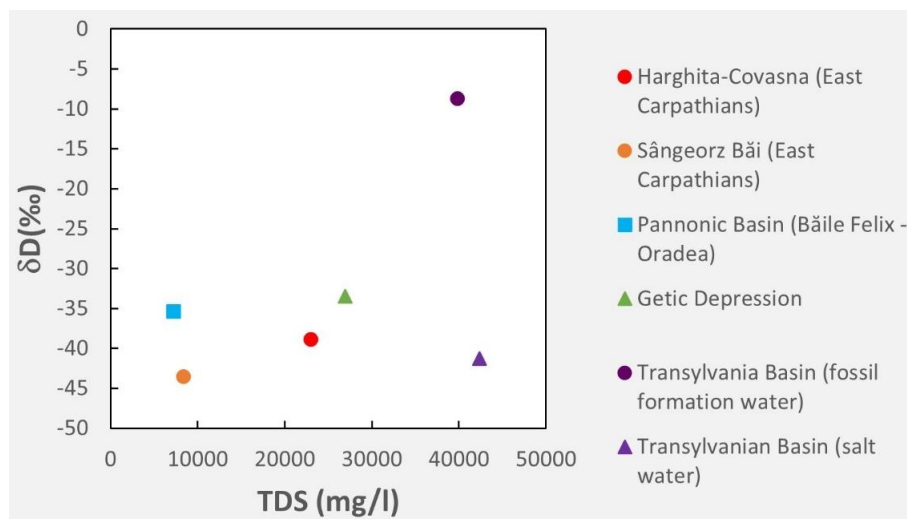


Figure 4. Plot of the mean values of (‰) and TDS (mg/l) of formation water in different areas from Romania

5. CONCLUSIONS

The mineral waters in the Olănești area are of deep origin, such as formation waters, in different stages of dilution with surface waters. The formation waters, highly mineralized (sulphurous, chloro-sodium, bromo-iodinated, ammoniacal, with low sulphate content) is mixed in different proportions with water of meteoric origin, accumulated in the Eocene conglomerates or Senonian sandstones with increased sulphates content. Based on δD data, three components have been identified: local infiltration waters, especially from the Olănești Valley, waters from high altitudes, and deep formation waters. The presence of H_2S is an important characteristic of the mineral waters from Olănești. The H_2S is considered of organic origin, resulting from the reduction of sulphates by specific anaerobic bacteria in the presence of hydrocarbons.

The application of isotopic and geochemical methods in the study of groundwater and in particular of mineral and geothermal waters, as well as the unitary interpretation of results in a geological, hydrogeological and geothermal context brings important clarifications regarding the origin and genesis of waters, input zones and recharge mechanisms, determination of residence times and underground flow rates, as well as estimation of mixing relationships between different adjacent aquifer systems. From a genetic point of view, groundwater is a mixture in varying proportions between two basic

components. The origin of these two components is markedly different; on the one hand there is the syngenetic component, such as formation water or fossil water, and the current component represented by the infiltration into the ground of some waters with an isotopic composition similar to the surface waters of meteoric origin. As such, knowledge of the isotopic composition of surface water and those from precipitation is indispensable in assessing the replenishment of groundwater aquifers.

Further studies, mainly based on the use of radioactive isotopes of hydrogen and carbon (tritium and radiocarbon) could bring more useful information about the aquifers (open or close system), the residence time and a better understanding of water-rock interactions (Făurescu et al., 2011; Făurescu et al., 2015; Bojar et al., 2021b; Papp, 2021).

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