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ASSESSING BARIUM AND STRONTIUM CONCENTRATIONS AND SPECIATION IN GROUNDWATER FROM THE AREA OF THE FUTURE WEAK – AND – MEDIUM RADIOACTIVE WASTE REPOSITORY SALIGNY – ROMANIA

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Abstract; We present herein our results regarding the barium and strontium concentrations and speciation in groundwater collected monthly (in July, August, September and October 2012) in the area of a future repository of weak and medium radioactive waste situated next to the village Saligny (Romania). By means of atomic absorption spectrometry with electrothermal atomization using a graphite furnace, it was established that all collected samples contained barium and strontium in various concentrations (Ba: 0.428 mg/L – 0.003 mg/L; Sr: 5.807 mg/L – 0.076 mg/L). Aqueous speciation calculations were performed by means of the PHREEQC software, by using the thermodynamic database LLNL (Lawrence Livermore National Laboratory). It was accordingly established that the prevalent chemical species were the Ba^{2+} and Sr^{2+} cations. Further on, a principal component analysis has been conducted to confirm that the results obtained are in agreement with the theoretical model.

Key words: alkaline earth metals, concentrations, speciation, groundwater, waste repository, Saligny

1. INTRODUCTION

Barium and strontium are elements which have long been known to be present in the aqueous environment (Bowen, 1956). There have been however, in the past, considerable difficulties in the analytical determination of these two elements. Strontium is very difficult to separate from calcium, especially in trace amounts, while barium is more easily separated, even if present in small amounts (Andersen & Hume 1968). The most popular analytical techniques used to determine barium and strontium in samples collected from various natural environments are atomic absorption spectrometry including flame (F – AAS) or graphite furnace (GF – AAS), and inductively coupled plasma mass spectrometry (ICP – MS) or optical emission spectrometry (ICP – OES), chiefly due to their capability of securing very small detection limits (Bowman & Willis 1967; Bishop, 1990; Gupta, 1991; Dalai & Sarin 2002). Strontium and barium in samples collected from natural environments can also be determined by using microwave digestion of the samples prior the ICP – OES determinations (Kutseva et al., 2000). X – ray fluorescence spectrometry can also be used with a low detection limit (Zawisza & Sitko 2006).

In the last decades in many countries significant progresses have been made in geological repository with the aim to solve the problem of a safe and acceptable solution for existing and future inventories of high-activity, long-lived radioactive waste. Worldwide, whatever is the existing nuclear fuel cycle, the geological repository is considered to be the better final solution.

In Romania, on the territory of Saligny village, a final repository for weak and medium active waste is considered for being developed in order to host radioactive waste derived from the Cernavodă Nuclear Power Plant (NPP) (Niculae et al., 2008;

Niculae et al., 2009). The low and intermediate level radioactive waste resulted from the operation of Cernavodă NPP include: compactable waste; non – compactable waste; organic liquids; spent filter cartridges and the low activity spent resins. The radioactive waste disposal needs to be carried out in a manner that provides an acceptable level of safety and which can be demonstrated to comply with the established regulatory requirements and criteria. Safe isolation of the radioactive waste depends on the performance of the overall disposal system, which is made up of three major components: the site, the disposal facility and the waste form. The suitability of a site will depend on its thorough characterization, in physical, chemical, hydrological and geochemical terms (Mocanu et al., 2007; Bucur et al., 2007). Potential contamination of the environment by various metal chemical species that originated in a radioactive waste repository is an investigation field which in recent years has made the object of intensive studies (Encian et al., 2013; Toma et al., 2007; Tudorache & Marin 2012; Zupunski et al., 2014).

In the case of CANDU type reactors, like those which operate within the Cernavodă Nuclear Power Plant, the radioactive waste is derived ensuing to contamination with the radionuclides: ^{134}Cs, ^{137}Cs, ^{131}I, ^{90}Sr, ^{141}Ce, ^{140}Ba, ^{95}Zn, ^{60}Co, ^{59}Ni, ^{63}Ni, ^{59}Fe, ^{51}Cr, ^{95}Zr, ^{95}Nb, ^{54}Mn, ^{99}Tc, ^{238}U, ^{239}Pu, ^{241}Am, ^{3}H, ^{14}C, etc. Taking into account that for a specific element, both its stable, and its radioactive isotopes exhibit almost identical chemical properties, as a consequence of their common electronic structure, it is also normal that their behavior is identical also with respect to natural geochemical process. This is the basic rationale underlying the present study, namely to determine some alkaline earth metals in groundwater, wich correspond to the radionuclides derived specifically from the CANDU type reactors. In this way, there can be anticipate the environmental diffusion pattern of the radionuclides existing within the stored waste.

In the light of the above considerations, the present work provides an evaluation of the concentrations and speciation of barium and strontium in groundwater samples collected from the area of the future radioactive waste repository at Saligny. To this end, we have tested an analytical approach for assessing barium and strontium concentrations by using atomic absorption spectrometry with electrothermal atomization. Aqueous speciation calculations were performed with the PHREEQC software and the enclosed LLNL (Lawrence Livermore National Laboratory) thermodynamic database.

2. EXPERIMENTAL SECTION

2.1. Hydrogeological setting

The low and intermediate level radioactive waste generated by the operation and decommissioning of Cernavodă Nuclear Power Plant are planned to be disposed into a new repository located on Saligny site. The highest elevation in this region reaches 72 m above the Black Sea level, and the main surface – water bodies are the Danube – Black Sea Channel and Ţibrinului Pond, the latter being located about 2 km to the north with respect to the study area.

Ensuing to investigations and monitoring activities conducted in that area, three distinct hydrogeological units have been identified at the Saligny site (Dogaru et al., 2010): the unsaturated zone – which extends from the ground surface down to the water table crossed by the drilled wells; the saturated zone of the local, assumedly confined aquifers, hosted by the Berriasian – Valanginian, Aptian, and Eocene formations; and the saturated zone of the aquifer hosted by the Quaternary formations, which is directly connected to the river Danube.

The unsaturated zone includes several successive layers, which from the ground surface downwards display a rather uniform distribution as follows: loessoid clayey dusts, loessoid dusty clays, red clays, and Pre – Quaternary clays. Each of these horizons exhibits various degrees of saturation (Danchiv et al., 2004). According to the investigation carried out by Durdun (2001), the geology of the regions is relative simple, shown schematically in the figure 1.

2.2 Sampling and analytical methods

For this study, groundwater samples have been collected monthly (in July, August, September and October 2012), from 10 drill holes, 2 domestic wells and from the river Danube (Fig. 2). Out of a total of 13 sampling sites, the Berriasian – Valanginian aquifer was sampled by 7 sites (the domestic well B 7 and the drill holes FS 27, GP – C, GP – V, FS 20, FC 25 and FC 22), the Aptian aquifer by 2 sites (the drill holes APT 2 and FC 17), the Quaternary and Eocene aquifers by one site each (the drill hole FS 9 and the domestic well in Cişmelei Valley respectively), while 1 site (the drill hole FS 24) sampled water mixtures derived from several aquifers, and 1 site sampled river water (from the Danube). Prior to collecting the samples, the wells were appropriately pumped, so that the stagnant water, if any, was completely removed from where it had been stored in the well assembly.

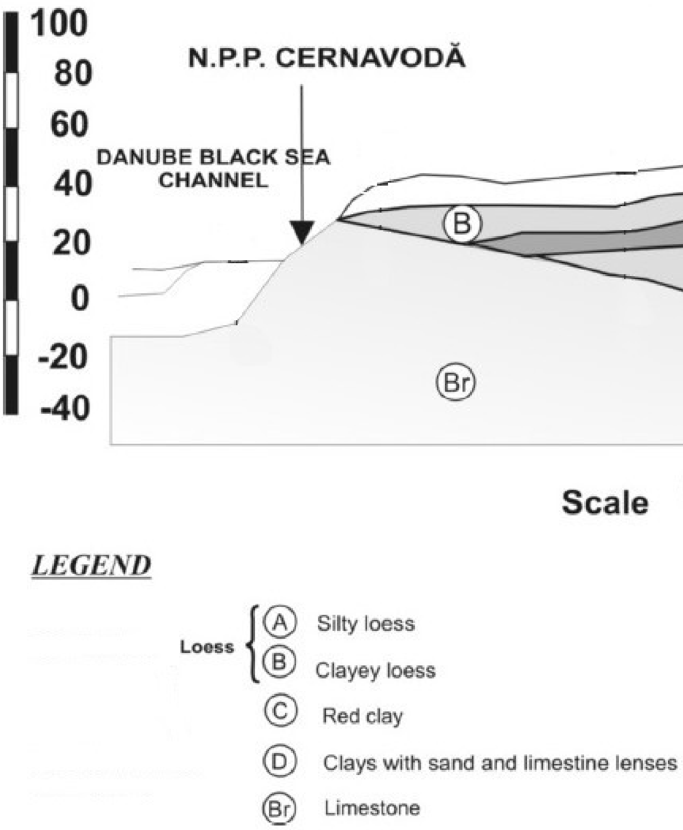

Figure 1 – Geological cross section of the study area

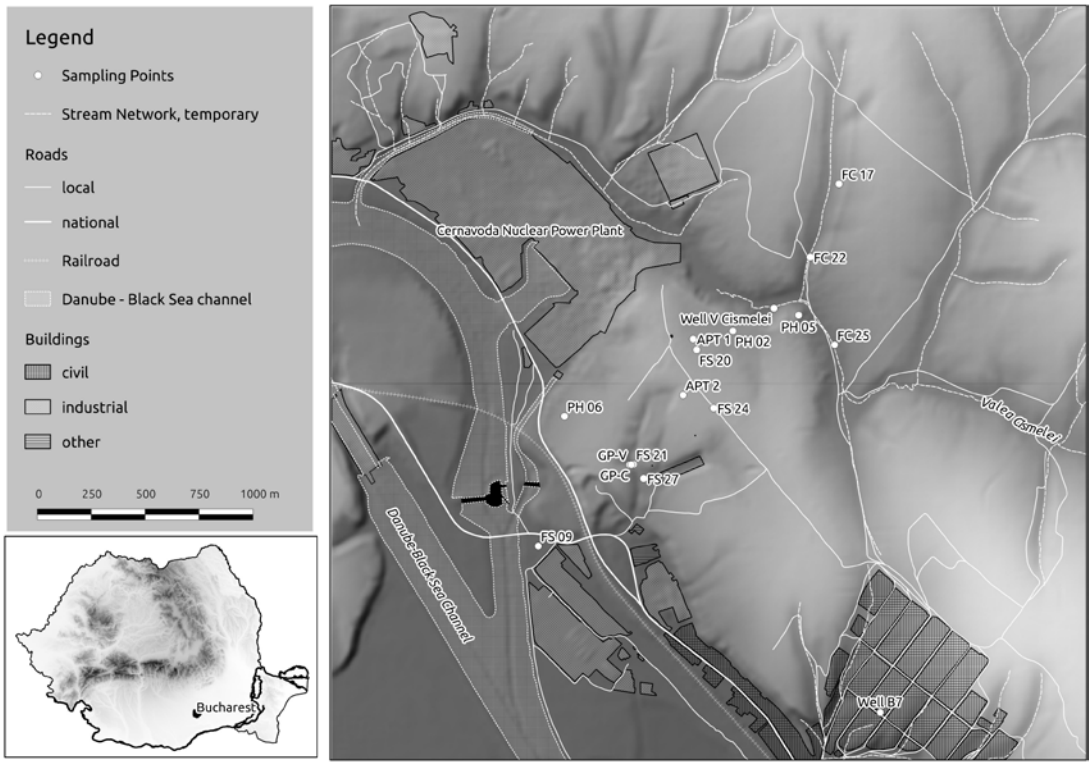

Figure 2 – Sampling sites

The determination of barium and strontium concentrations was performed with a Perkin – Elmer atomic absorption spectrometer, model AAnalyst 700, provided with a deuterium arc background correction, equipped with an AS – 800 autosampler, HGA – 800 graphite furnace, and a Lumina Single – element HCL – Barium and HCL – Strontium source lamp (Perkin – Elmer). The corresponding instrumental settings and operating parameters are listed in Table 1.

The graphite furnace temperature programs were carried out according to the manufacturer recommendations. The injected sample volume was 20 µL. In the case of strontium determinations, certain samples (drill hole APT 2, domestic wells B 7 and Cişmelei valley) required preliminary dilutions, since the dilution capability of the auto – sampler was exceeded. The calibration lines were traced by using solutions prepared from standard solutions CertiPUR® (Merck). All the solutions were prepared with ultra –pure water (TKA Ultra Pure System Gen – Pure; electric resistance 18.2 MΩ cm). In Table 2 there are listed the analytical performances of both methods; they were determined according to the international rules (ICH Q2A 1994; ICH Q2B 1996), by using the certified reference materials provided by NIST: Trace Elements in Water SRM 1643f.

The distinct steps involving sampling, samples storage and preparation, as well as in situ measurements (pH, Eh and temperature) have been completed in accordance with previously described procedures (Tudorache & Marin 2012). The total dissolved solids (TDS) content of each collected sample was calculated by summing up the concentrations of all the major cations and anions. The Na, K, Mg and Ca concentrations were determined in laboratory by means of standard flame – atomic absorption spectrometry methods (ISO – 1 1993; ISO – 2 1993; SR EN ISO 2002). The determinations were carried out with a Perkin – Elmer atomic absorption spectrometer, model AAnalyst 700. The water total alkalinity was determined by titration with a 0.05 N HCl solution, on unfiltered samples, within a time – interval of no more than 24 hours after sampling (SR ISO 2002). Nitrate was analyzed by a UV spectrometric method (Rennie & Sumner 1979). Sulfate was determined turbidimetrically (American Society for Testing and Materials 1995). The chloride was analyzed by the mercury (II) thyocyanate spectrophotometric method (Florence & Ferrar 1971). These determinations have been conducted by means of a molecular absorption spectrometer in the visible and ultraviolet spectra, of the Perkin – Elmer Lambda 25 model. The speciation calculations have been performed by means of the PHREEQC software (Parkhust & Appelo 1999).

3. RESULTS AND DISCUSSION

3.1. General hydrochemistry

The analyzed water samples physical–chemical parameters and the analytical results concerning the main cation and anion concentrations are indicated, in terms of minimum, maximum and mean values, in Tables 3 and 4. Sampling site number 10 (drill hole FC 25) was investigated only once, in July 2012.

The obtained analytical results indicate that the groundwater samples collected from the area of the future repository of weak and medium radioactive waste at Saligny are neutral to alkaline, with a maximum pH value of 10.31, that was recorded for the sample collected from the drill hole FC 17 (sampling site number 13).

Table 1 – Instrumental settings and operation parameters for the GF – AAS determination

Element Parameter	Barium	Strontium
Lamp type	HCL	HCL
Wavelength (nm)	553.6	460.7
Slit (nm)	0.2	0.7
Applied current (mA)	25	20
Energy lamp	25	20
Graphite tube	without platform	without platform
Calibration points (µg/L)	20; 60; 120	5; 15; 30
Matrix modifier (5 µL)	0.1 % $Ca(NO_3)_2$	–

Table 2 – Analytical performance for the GF – AAS determination of Ba and Sr in groundwater samples

Element Parameter	**Barium**	**Strontium**
Limit of detection (µg/L)	2.42	0.67
Limit of repeatability (µg/L)	5.32	3.53
Limit of reproducibility (µg/L)	4.88	4.19
Bias (%)	6.59	6.46
Recovery (%)	89.6 – 104.5	94.9 – 109.2

The average TDS values range between 0.11 g/L and 2.44 g/L, hence indicating that groundwater in this area is in general fresh, still with certain samples falling close to the transition toward brackish water. The bicarbonate ion, which is present in groundwater as a result of the dissolution of carbonate minerals such as dolomite and calcite, is the second anion (in terms of abundance) detected in the analyzed water samples, with a maximum concentration of 456 mg/L recorded in the sample collected from the drill hole APT 2. The maximum calcium and magnesium concentrations, of 186.1 mg/L and 203 mg/L respectively, exceed the corresponding WHO standards (World Health Organization 2006). In normal groundwater systems, the origin of these cations is mainly related to the corresponding carbonate minerals and to the dissolution and deposition processes in which the latter are involved. Sodium and potasium average concentrations range between 11.3 mg/L – 376.5 mg/L, and 0.5 mg/L – 68.8 mg/L respectively. Sodium in groundwater is largely controlled by saline intrusions, by evaporites leaching and by silicate minerals dissolution. In the groundwater samples from the study area, the chloride ion is the dominant anion, with a maximum concentration of 1355.8 mg/L, recorded in the sample collected from the drill hole APT 2.

Most samples in the study area exceeded the drinking water maximum admissible concentration for the nitrate ion (50 mg/L). The high nitrate ion concentrations are likely related to wastewater leakage associated to industrial activities, to urbanization and to agricultural practices. Sulfate in the study area varied between 0.4 mg/L – 1168.6 mg/L; the main origins of sulfate are gypsum dissolution and anthropogenic activities.

3.2. Barium and strontium concentrations and speciation

The results obtained for the barium and strontium determination by means of GF – AAS are presented in Table 5 and they show that all collected samples contain, in various concentrations, these alkaline earth metals.

Barium concentrations in the study area groundwater were found to range between 0.428 mg/L and 0.003 mg/L. Only samples taken in October from the drill holes FC 22 and FC 17 displayed barium concentrations that fell below the detection limit (LoD = 2.42 μg/L ≈ 0.003 mg/L). The corresponding variability is not likely to be of anthropogenic origin.

Generally, the barium content of the world groundwaters is low (less than 1 mg/L), and it is strongly controlled by the abundance of element in the bedrock, in relationship with clays and carbonate minerals (Mokrik et al., 2009). The low solubility of barium – bearing minerals, especially barite (BaSO4), inhibits the release of large amounts of barium in the groundwater; therefore, the concentration of dissolved sulfate in groundwater is an important control on the concentration of dissolved barium (Dowling et al., 2003). Strontium concentrations in the study area groundwater were found to range between 5.807 mg/L and 0.076 mg/L, the maximum value being reached in the sample collected from the drill hole APT 2 in August 2012.

Table 3 – The physical – chemical parameters of the analysed water samples; sampling site: 1 – Danube; 2 – domestic well B 7; 3 – drill hole FS 9; 4 – drill hole FS 27; 5 – drill hole GP – C; 6 – drill hole GP – V; 7 – drill hole FS 24; 8 – drill hole APT 2; 9 – drill hole FS 20; 10 – drill hole FC 25; 11 – domestic well Cişmelei valley; 12 – drill hole FC 22, and 13 – drill hole FC 17

Site	**T (^{o}C)**			**pH**			**Eh (mV)**			**TDS (g/L)**		
Site	**min.**	**max.**	**mean**	**min.**	**max.**	**mean**	**min.**	**max.**	**mean**	**min.**	**max.**	**mean**
1	14.5	26.9	20.6	7.85	8.42	8.02	102	189	153	0.24	0.33	0.28
2	13.2	13.4	13.3	7.40	7.81	7.52	43	220	144	1.09	1.17	1.12
3	17.1	18.4	17.8	7.28	7.59	7.45	-112	-49	-86	0.47	0.56	0.52
4	14	15	14.3	8.31	9.33	8.80	20	89	64	0.38	0.63	0.56
5	13.6	14.2	13.8	7.27	7.32	7.30	135	215	175	0.68	0.72	0.69
6	13.6	14	13.8	7.24	7.61	7.39	111	197	151	0.66	0.73	0.70
7	13.4	13.9	13.7	9.12	9.20	9.15	88	155	118	0.11	0.14	0.13
8	13.2	13.5	13.4	7.37	7.56	7.46	168	216	192	1.60	2.44	1.92
9	13.2	13.9	13.6	8.41	8.83	8.66	-121	166	62	0.24	0.30	0.27
10	13.1	13.1	13.1	7.28	7.28	7.28	-18	-18	-18	0.96	0.96	0.96
11	12.8	15.6	14.1	7.41	7.62	7.54	86	219	141	1.28	1.39	1.36
12	13.4	13.7	13.6	7.28	7.42	7.35	-16	178	82	0.47	0.69	0.63
13	13.3	13.6	13.4	9.39	10.31	9.84	17	57	33	0.11	0.13	0.12

That circumstance is suggesting the possibility that this element has migrated toward the Aptian aquifer. This could be a consequence of the fact that in aqueous environments where pH was at or below neutrality (so that precipitation with the naturally occurring anions was at the minimum), and where the soil ion – exchange capacity was limited, strontium was very mobile and the extent of migration was determined by the flow of water (Davidson et al., 2005).

Saxena et al., (2004) have suggested that the Sr content could be used for distinguishing between various water types. They indicated Sr value – ranges of < 1.6 mg/L for fresh groundwater, 1.6 mg/L – 5.0 mg/L for brackish water, and > 5.0 mg/L for saline groundwater in the coastal aquifers. The Sr values obtained in this study show that the groundwater samples fall within the fresh groundwater class; only samples from the drill hole APT2 belong to the brackish water category.

In natural waters, barium and strontium could generate chemical species that occur in a variety of percentages. These species cannot be identified ensuing to the simple analysis of groundwater, and they can only be computed by means of dedicated software, like PHREEQC. The input data in this study were: temperature, pH, Eh and concentrations of barium, strontium and main cations and anions (Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-}, Cl^- and NO_3^-). Thus, under the concerned geochemical conditions, barium and strontium species concentrations computed for all the analyzed water samples showed that the chemical species with the highest percentage of occurrence were the Ba^{2+} ion (99.24 ± 0.44) % and the Sr^{2+} ion (90.21 ± 7.16) %. Mobility of these main species is primarily controlled by sorption reactions with aquifer sediments (Santoni et al., 2016). Other studies show that Sr^{2+} mobility in natural environments is reduced by the presence of competing divalent cations with smaller ionic radius, such as aqueous Ca^{2+} and Mg^{2+}, while the mobility of Sr^{2+} is reported to be less affected by the presence of monovalent cations such as Na^+ and K^+ (Hull & Schafer 2008). This is relevant to nuclear sites, where the ionic strength of contaminant plumes is often high (Wallace et al., 2012). The tendency of barium and strontium to form inorganic species is very limited, the consequence being that besides those main species (Ba^{2+} and Sr^{2+}), the water samples also include much smaller percentages of the following chemical species: $BaNO_3^+$ (0.41 ± 0.35) %, $BaCO_3$ (0.31 ± 0.40) %, $BaCl^+$ (0.046 ± 0.019) %, $BaB(OH)_4^+$ (0.003 ± 0.005) %, $BaOH^+$ (0.0006 ± 0.0001) %, $SrSO_4$ (8.84 ± 7.41) %, $SrCO_3$ (0.45 ± 0.66) %, $SrNO_3^+$ (0.42 ± 0.61) %, $SrCl^+$ (0.082 ± 0.035) %, and $SrOH^+$ (0.007 ± 0.002) %. Similar results have been obtained also in other studies (Tudorache et al., 2010).

3.3. Statistical approach

The data obtained in this study have been analyzed by means of the principal component analysis (PCA) methodology, in order to outline for the concerned data-set correlations, as well as patterns. First, the scree plot (Fig. 3) showed that 12 components could be rationally used to explain the variation of the obtained data.

Second, the loading plot (Fig. 4) illustrates the correlation among the parameters under investigation and the data obtained. It is obvious that pH is one of the main factors that influence the existence of the $BaOH^+$ and $SrOH^+$ species: a high correlation was obtained between pH and the concentration of these two species. In addition, temperature acts in the same way, being responsible for the existence of the above-mentioned species in solution. Moreover, the same plot indicates that also $SrCO_3$ is related with pH and temperature.

Contrary to strontium carbonate, $BaCO_3$ follows a different pattern, being less correlated with pH and temperature. By computing the Pearson correlation coefficient for the pairs of variables ($SrOH^+$ concentration, pH), ($BaOH^+$ concentration, pH), ($SrCO_3$ concentration, pH) and ($BaCO_3$ concentration, pH), the following values have been obtained: 0.592, 0.212, 0.125 and - 0.306, respectively. The positive values for the Pearson coefficient range between 0 and 0.6, indicating a better fitting distribution for the variables (Ba concentration, bicarbonate ions concentration) than for the (Ba concentration, pH) ones. These results are in agreement with the theoretical model which postulates that if the pH increases above 11, Ba^{2+} ions form the barium hydroxide, $Ba(OH)_2$, which is moderately soluble in water. The groundwater pH reaches such values when natural or anthropogenic disasters occur. The presence of bicarbonate ions in the groundwaters under investigation ensures the existence of Ba^{2+} in solution as $Ba(HCO_3)_2$, which is a highly soluble salt. The Pearson correlation of - 0.306 shows that Ba^{2+} and sulfate ions are not correlated, meaning that if the concentration of sulfate ions increases in solution, the Ba^{2+} becomes $BaSO_4$ a white precipitate, hardly soluble in water. The score plot (Fig. 5) displays a highly compact group and a few isolated sampling points. Among the latter, the drill holes APT 2 and FC 17 belong to the same aquifer, namely Aptian, while the drill holes FS 20, FC 22 and FC 25 belong to another aquifer, hosted by Berriasian – Valanginian formations. The statistical differences outlined for these drill holes could be explained by anthropic activities (introduction of allochthonous water during workover operations). A particular behavior was noticed for the domestic well in Cişmelei walley and drill hole FS 9 which taps the Eocene aquifer.

Table 4 – Chemical composition of the analyzed water samples (sampling sites codes are the same as in Table 3; all results are expressed as mg/L)

ANIONS												
Site	**HCO_3^-**			**SO_4^{2-}**			**Cl^-**			**NO_3^-**		
	min.	**max.**	**mean**	**min.**	**max.**	**mean**	**min.**	**max.**	**mean**	**min.**	**max.**	**mean**
1	138.8	190.4	160.9	16.6	40.2	30.5	17.7	77.0	45.9	20.9	22.2	15.5
2	301.2	306.0	303.2	381.1	456.9	411.8	422.5	451.8	440.2	182.6	190.5	185.5
3	303.0	366.0	335.4	23.7	44.2	35.2	61.3	83.0	80.6	9.7	31.0	20.5
4	53.2	237.6	183.7	164.9	185.5	172.6	231.3	270.1	252.9	28.8	109.0	78.8
5	301.1	313.7	307.1	156.3	173.6	161.4	196.6	269.8	238.1	22.2	28.4	26.0
6	232.5	300.0	265.6	196.0	210.4	204.4	268.5	280.7	274.3	32.8	41.6	38.9
7	52.4	74.4	64.9	0.4	4.9	2.0	91.3	112.2	103.4	8.4	17.7	15.1
8	359.7	456.0	414.8	610.7	1168.6	828.9	491.5	1355.8	858.7	78.5	294.8	135.4
9	112.5	135.8	126.7	1.4	4.5	3.4	197.1	259.7	236.5	29.2	162.5	85.3
10	437.0	437.0	437.0	224.6	224.6	224.6	373.3	373.3	373.3	44.7	44.7	44.7
11	419.6	427.2	422.6	424.3	516.7	489.0	327.1	380.0	358.6	122.3	137.8	130.4
12	273.5	282.9	278.5	45.9	103.8	87.3	156.2	276.6	231.4	27.5	43.6	39.0
13	13.3	18.5	15.7	1.9	6.8	3.7	395.2	430.7	408.0	5.3	12.4	8.8
CATIONS												
Site	**Na^+**			**K^+**			**Ca^{2+}**			**Mg^{2+}**		
	min.	**max.**	**mean**	**min.**	**max.**	**mean**	**min.**	**max.**	**mean**	**min.**	**max.**	**mean**
1	11.3	22.2	15.5	2.6	3.1	2.8	40.7	52.2	45.7	9.6	13.8	11.5
2	140.7	144.6	142.7	3.0	3.3	3.2	143.0	147.2	145.0	61.0	67.2	62.8
3	34.3	45.9	40.5	2.9	3.4	3.2	47.7	61.5	52.1	28.8	34.9	31.6
4	68.4	73.1	71.7	4.8	11.1	7.1	32.2	75.9	58.8	24.3	47.0	39.5
5	62.3	68.9	65.4	1.3	1.6	1.5	102.4	107.4	105.0	36.1	41.7	38.9
6	68.5	74.1	71.1	1.7	2.0	1.8	92.4	101.8	97.6	38.9	40.8	40.2
7	17.2	20.7	18.8	14.3	16.1	15.4	7.9	16.1	13.6	2.9	3.2	3.1
8	268.8	376.5	313.1	33.0	68.8	57.4	82.3	186.1	126.9	89.9	203.0	139.2
9	63.9	75.2	69.3	14.9	16.0	15.6	15.9	17.6	16.6	1.6	1.9	1.7
10	77.7	77.7	77.7	1.8	1.8	1.8	130.3	130.3	130.3	75.0	75.0	75.0
11	208.3	225.4	216.9	1.2	1.4	1.3	103.8	118.6	108.5	77.6	91.2	84.2
12	16.1	22.5	19.1	0.5	1.8	0.9	88.8	146.8	127.5	26.7	43.9	36.1
13	46.3	57.6	53.6	2.5	2.8	2.6	23.2	34.9	28.8	10.2	11.6	11.1

Table 5 – Barium and strontium concentrations in the water samples (sampling sites codes are the same as in Table 3; all results are expressed as mg/L; n.a = not analyzed; LoD = limit of detection)

Element	**Barium**					**Strontium**			
Month Site	**Jul-2012**	**Aug-2012**	**Sep-2012**	**Oct-2012**		**Jul-2012**	**Aug-2012**	**Sep-2012**	**Oct-2012**
1	0.031	0.023	0.035	0.034		0.273	0.284	0.612	0.617
2	0.050	0.037	0.041	0.079		1.462	1.530	1.567	1.658
3	0.080	0.075	0.099	0.089		0.564	0.590	0.762	0.801
4	0.053	0.047	0.014	0.110		0.881	0.965	0.880	0.485
5	0.072	0.061	0.076	0.066		0.954	1.009	1.052	1.008
6	0.047	0.045	0.102	0.085		1.109	1.014	1.215	1.244
7	0.003	0.008	0.009	0.010		0.076	0.108	0.238	0.254
8	0.022	0.059	0.024	0.140		5.051	5.807	2.262	1.851
9	0.084	0.068	0.034	0.101		0.275	0.279	0.384	0.404
10	0.230	n.a	n.a	n.a		1.254	n.a	n.a	n.a
11	0.021	0.023	0.428	0.024		1.445	1.507	1.445	1.400
12	0.076	0.020	0.135	<LoD		0.821	0.624	0.651	0.630
13	0.028	0.017	0.021	<LoD		0.356	0.381	0.565	0.741

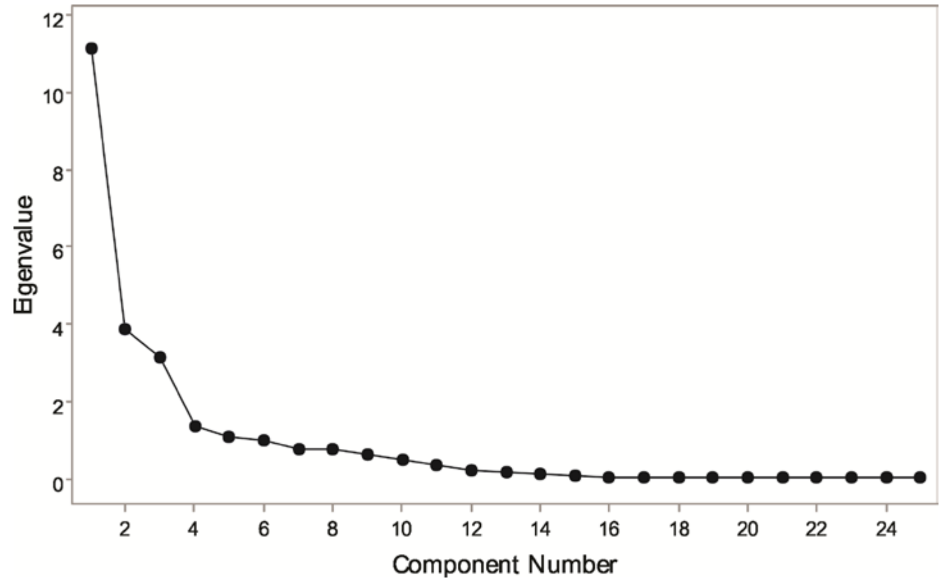

Figure 3 – The results obtained by means of PCA: the scree plot

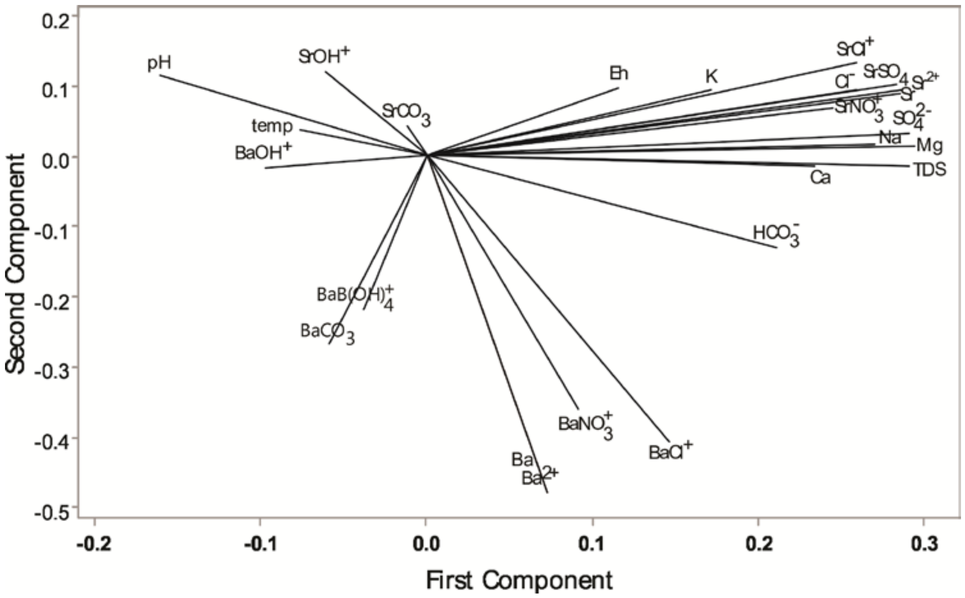

Figure 4 – The results obtained by means of PCA: the loading plot

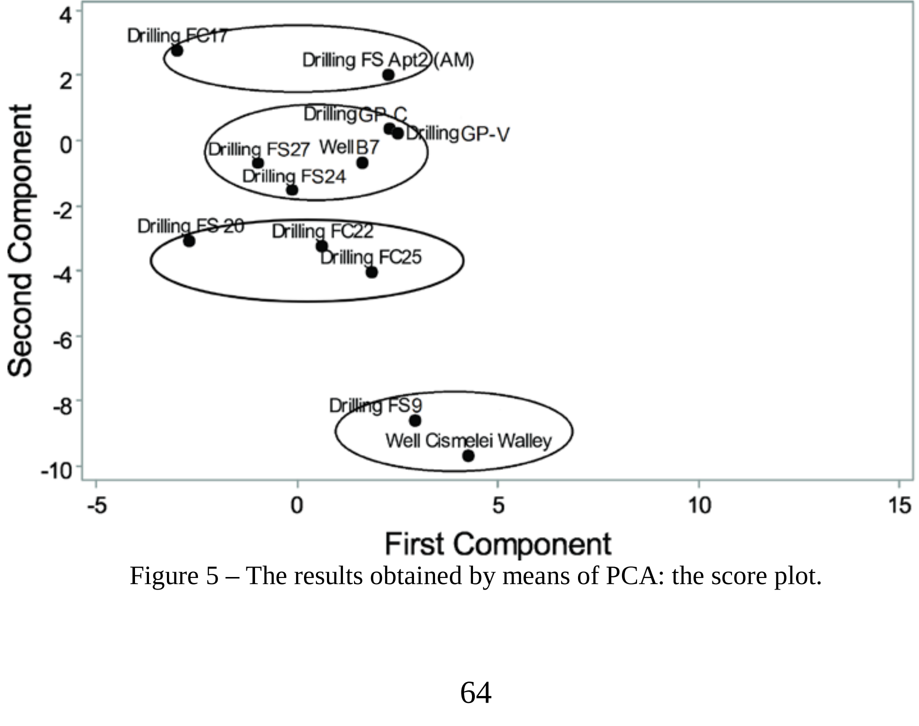

Figure 5 – The results obtained by means of PCA: the score plot.

In agreement with the data obtained, in the future, the environmental diffusion pattern of the radionuclides existing within the stored waste can be anticipate.

4. CONCLUSIONS

The barium and strontium concentrations in the groundwater of the study area have been analyzed by using atomic absorption spectrometry with electrothermal atomization. Our analysis has indicated a wide range of barium and strontium concentrations in the analyzed waters. The largest concentration of strontium (5.807 mg/L) was recorded in the sample collected from the drill hole APT 2 in August 2012. Only samples collected in October from the drill holes FC 22 and FC 17 had barium concentrations below the detection limit (2.42 µg/L).

The barium and strontium speciation for the investigated water types is simple and predictable. Under natural geochemical conditions, barium and strontium exist almost exclusively in the divalent state, as Ba^{2+} and Sr^{2+}. Besides these ions, much smaller percentages of other chemical species are present as well: $SrSO_4$, $SrCO_3$, $SrNO_3^+$, $SrCl^+$, $SrOH^+$, $BaNO_3^+$, $BaCO_3$, $BaCl^+$, $BaB(OH)_4^+$ and $BaOH^+$.

A statistical approach that used principal component analysis showed that the $BaOH^+$ and $SrOH^+$ species were strongly correlated with pH and temperature.

In the future, based on the results, we can determine mechanisms that influence the migration of radionuclides in radioactive waste repositories.

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