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FACULTY OF ENVIRONMENTAL SCIENCE

UNDERGROUND WATER DATING AND AGE CORRECTIONS USING RADIOCARBON

- Summary of the PhD Thesis -

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Thesis content

INTRODUCTION

Radiocarbon natural production takes place in high layers of the atmosphere due to reactions between cosmic rays and nitrogen atoms with abundance, $^{14}C/^{12}C$, in the order of 10^{12}:

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{14}_{6}C + ^{1}_{1}p$$

^{14}C thus formed oxidises to carbon dioxide and results a constant flux of $^{14}CO_2$ in troposphere where is incorporate in plants through photosynthesis, as well with meteoric waters and oceans through CO_2 exchange reactions (figure 1). Majority of this ^{14}C incorporated in plants goes back in atmosphere through plant decomposition and roots respiration. Radiocarbon in the soil can be taken into solution as dissolved inorganic carbon ($DIC = CO_{2(aq)} + HCO_3^- + CO_3^{2-}$) or as dissolved organic carbon. By consequence, any carbon compound derived from atmospheric CO_2 is potentially eligible for radiocarbon dating.

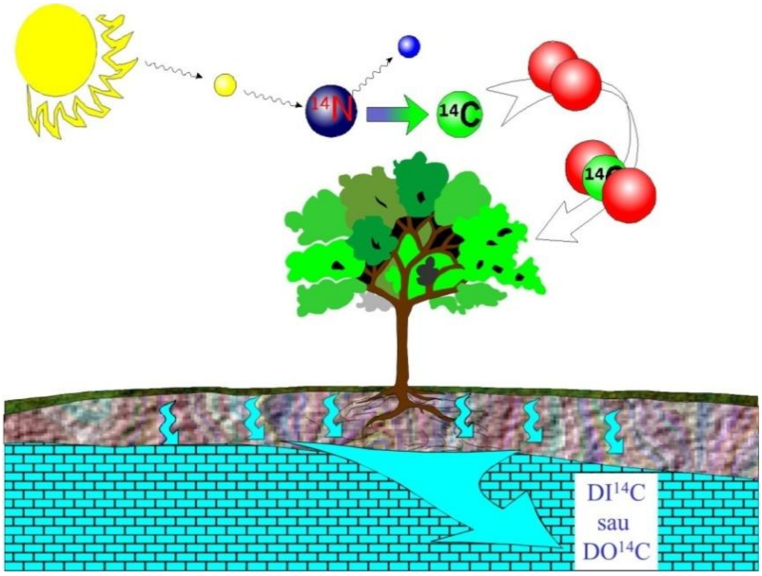

Figure 1. The pathway of ^{14}C during photosynthesis, respiration in soil and dissolution by underground waters

Williard Frank Libby won the Nobel Prize in 1960 for developing radiocarbon dating method. First attempts to confirm the methods were done using samples with known age from Ancient Egypt. Experiments done to develop this method used acacia wood from Djoser Pharaoh (Third Dynasty, with known age between 2700 and 2600 BC). Libby's theory says that if the half-life of ^{14}C is 5568 years, the radiocarbon concentration found in the sample will be approximately 50% of the concentration found in the wood today. Results confirmed this hypothesis. Were carried out other analyzes on several types of wood dated by dendrochronology method, which confirmed, with an uncertainty of + /- 10%, Libby's theory. Experiments carried out suggested that the half-life was determined quite accurately, but also have imposed another hypothesis; in fact invalidated later that atmospheric radiocarbon concentration remained constant over time.

Soon method was accepted as scientific instrument and until the late '50s were developed 20 laboratories that used 14C dating. Further experiments demonstrated that the half-life used Libby was about 3% lower than in reality, the true value of 5730 + /- 40 years being known as the Cambridge half-life.

Due to its long half-life radiocarbon is very important for dating, and is now used extensively in hydrology to underground water dating. In the last decade methods for determining the ^{14}C concentrations were significantly improved and that why radiocarbon dating is widely used worldwide.

All experiments required to elaborate this thesis were conducted in Tritium Laboratory of the National Research and Development Institute for Cryogenic and Isotopic Technologies - ICSI Rm.Valcea. I work in this laboratory for more than eight years, and concerns of research team include the theme of this PhD thesis. Laboratory was part over time in many projects under the national framework of research, one example being the project *"Use and development of new methods for investigating and dating of major changes in climate and sea level in the Danube Delta and Black Sea in order to reconstruct the evolution and forecasting associated risks (CLIMARISC)"*.

By this PhD thesis entitled "**UNDERGROUND WATER DATING AND AGE CORRECTIONS USING RADIOCARBON**" I try to determine the age of an aquifer from territory of the town Băbeni, Valcea.

Proposed objectives to solve in this research were optimization and validation of the method used for the sample preparation and determination of ^{14}C concentration in water samples and on the other hand applying of age correction models. Another objective of this thesis was to correlate environmental isotopes (^{14}C, ^{3}H, ^{18}O and ^{2}H) to estimate recharge conditions of studied aquifer.

The method used to preparation of samples is the direct absorption method, which seeks principles similar to those of benzene synthesis method. Working procedures involve following stages: preparation of scintillation cocktail by our own recipe; precipitation of dissolved inorganic carbon (DIC) in form of barium carbonate; acidification of barium carbonate to obtain CO_2 followed by CO_2 absorption into scintillation cocktail and determination of ^{14}C specific activity using an ultra-low level liquid scintillation spectrometer Quantulus 1120. Chemical and isotopic analyzes were made in specific laboratories of ICSI Rm. Valcea respectively Chemistry Laboratory and Laboratory of physicochemical characterization, environmental and food quality. Modeling undertaken for identifying potential species and saturation indices of water samples was done with the software PHREEQC 2.10, and for modeling of underground water age was used interactive software NETPATH (C) 2009. These programs were developed by U.S. Geological Survey.

This thesis is structured in seven chapters. **The first chapter** is devoted to a brief introduction that summarizes topic, methods used, and the objectives of the thesis and a short description of each chapter.

In the **second chapter**, *"Carbon cycle in nature"*, I presented succinctly carbon isotopes and global carbon cycle with the emphasis on properties and terminology used in literature. It basically shows carbon reservoirs (atmosphere, terrestrial biosphere, hydrosphere and lithosphere) and how they are related to each other in such a way to maintain a steady state in each of the reservoirs considered, total carbon content remains constant, losses being offset by exchange with other reservoirs.

In the **third chapter**, *"^{14}C behavior in underground water"*, I presented the evolution of carbon in underground water and described in detail geochemistry of carbonates. I also detailed how to use the software PHREEQC 2.10. to model chemical processes in water.

In the **fourth chapter**, *"Underground water dating and age correction models"*, I described how to do the reporting of ^{14}C activities and concentrations, the dating methods for identifying modern and old underground water. I also presented some of correction models that currently use and how to use NETPATH software for modeling groundwater age.

The fifth chapter, *"Determination of ^{14}C specific activity using liquid scintillation method"* includes a brief analysis of radiocarbon techniques and methods of sampling and sample preparation for determination of the specific activity of ^{14}C. The last part of this chapter I have presented in detail liquid scintillation method and some personal contribution namely regarding optimization and validation of the method.

T**he sixth chapter**, entitled *"Dating of one aquifer from Băbeni-Vâlcea area and age corrections using radiocarbon"* presents the experimental, original, focused on a series of measurements and analyzes to determine the age of an aquifer from territory of the town Băbeni, Vâlcea. For this were collected and analyzed samples from 8 drillings of Olt River Administration, 3 domestic wells and the main rivers in the area, Olt River and Bistrita River. Also this chapter presents the results identified by applying the age-correction models and was estimated recharge conditions of studied aquifer by correlation of environmental isotopes (^{14}C, ^{3}H, ^{18}O and ^{2}H).

The last part of the thesis, namely **the seventh chapter** entitled "*Conclusions and Perspectives*" brings together preliminary conclusions drawn at the end of each chapter. Although the thesis develops an actual and modern theme it remains open to continue with further research after the completion of this work.

PhD thesis ends with references, very precise targeting theme of underground water dating age corrections using radiocarbon, focusing on recent studies in this field.

Part of ideas, discussions and results of this thesis have been exploited by the publication of four articles published in ISI journals and over 15 papers at national and international conferences.

DATING OF ONE AQUIFER FROM BĂBENI-VÂLCEA AREA AND AGE CORRECTIONS USING RADIOCARBON

Studied aquifer is located in the city Băbeni, Valcea county, and the drillings from which water samples were collected belong to Olt River Administration. Drilled in the early 1970s these wells are used to monitor groundwater levels in this area and also monitoring the chemical composition of water in order to identify possible sources of aquifer pollution.

From morphologically and structurally point of view Băbeni city territory ($24^0$30'E, $45^0$00'N) is part of Valcea Subcarpathians, which in turn are part of the morphostructural area of Getic Plateau.

To fulfill the objectives of this thesis I collected water samples from eight drillings, three domestic wells located further along flow path of aquifer and also from the two main rivers that influence groundwater body, respectively Olt river and Bistrita river. For drillings were preserved original names, which are noted from F1 to F8, and wells were marked with A, B, C in order of water sampling.

Table 1. Geographical coordinates of the sampling locations

Location	**Latitude**	**Longitude**	**Depth (m)**
Drilling F1	44°58'45.79"N	24°16'57.39"E	15
Drilling F2	44°58'54.19"N	24°16'37.73"E	20.5
Drilling F3	44°59'16.03"N	24°16'11.91"E	10.5
Drilling F4	44°59'17.81"N	24°15'55.45"E	12
Drilling F5	44°59'11.76"N	24°15'10.90"E	17.1
Drilling F6	44°58'39.67"N	24°14'40.10"E	11.5
Drilling F7	44°58'34.13"N	24°14'40.22"E	15
Drilling F8	44°58'19.24"N	24°14'38.88"E	18
Well C	44°58'6.57"N	24°14'34.19"E	~7
Well B	44°57'42.25"N	24°14'32.90"E	~9

Well A	44°56'29.42"N	24°14'21.36"E	~10
Olt River	44°58'54.22"N	24°16'49.59"E	-
Bistrița River	44°58'32.81"N	24°14'50.06"E	-

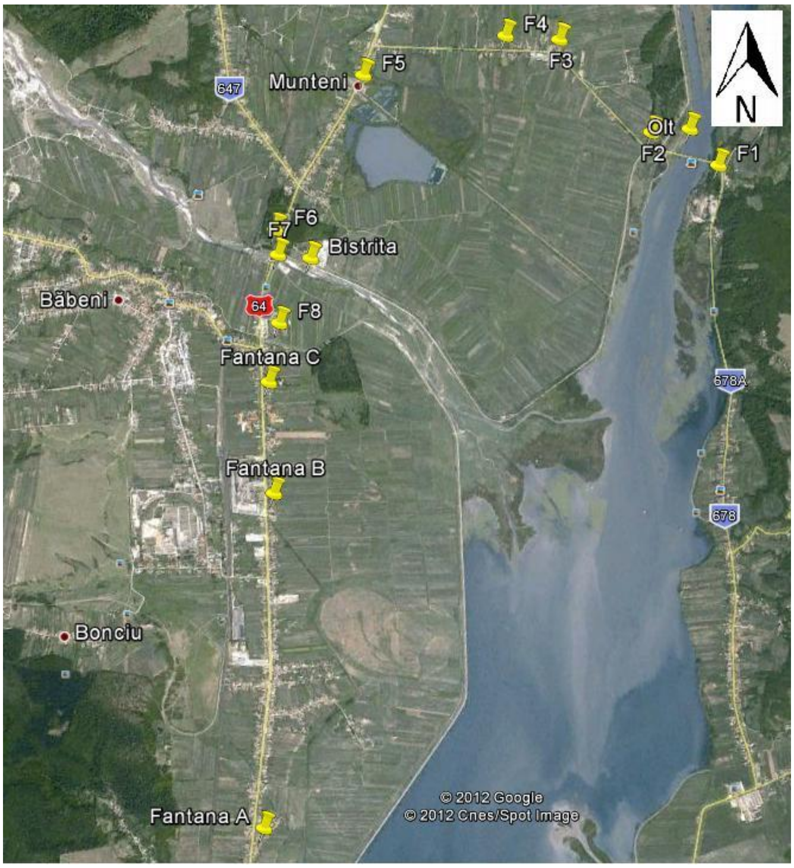

Figure 2. Map of sampling locations (built with Google Earth 2012)

Drilling F1 is located on the left side of the Olt River in the vicinity of the bridge located on County Road 678A that connects city Băbeni with commune Galicea. Lithological description of this drilling indicates that layers sequence through which drilling F1 pass is: brown topsoil, medium-course purple sand, coarse sand with gravel, coarse sand with rare gravel, yellowish sandy clay, low compact purple clay, purple yellow loamy sand, purple micaceous sand, yellow sand with water, coarse sand with gray gravel rare items, coarse sand and purple gray gravel, low compact purple yellowish clay.

Drilling F2 is located on the left side of the County Road 678A at a distance of 500 meters from drilling F1. Lithological description of this drilling indicates that layers sequence through which drilling F2 pass is: brown topsoil, boulders and yellowish white gravel, purple sandy clay, low compact yellow clay, low compact purple clay, purple micaceous sand, gravel and coarse purple yellowish sand, low compact purple clay.

Drilling F3 is located on the left side of the County Road 678A that connects city Băbeni with commune Galicea at a distance of 890 meters from drilling F2. Lithological description of this drilling indicates that layers sequence through which drilling F3 pass is: brown topsoil, boulders and coarse and medium sand, boulders with coarse and medium sand items, yellowish coarse sand, coarse sand with yellowish gravel, sandy purple clay.

Drilling F4 is located on the left side of the County Road 678A at a distance of 370 meters from drilling F3. Lithological description was not available and therefore age calculations for this considered that drilling F3 and F4 are identical due to small distance between them.

Drilling F5 is located on the right side of the National Road 64 that connects Rm. Valcea and Dragasani at a distance of 1000 meters from drilling F4. Lithological description of this drilling indicates that layers sequence through which drilling F5 pass is: brown topsoil, coarse yellowish sand, sandy purple clay and purple sand, coarse sand with boulders, compact yellowish purple sandy clay, purple sand, coarse sand, medium gravel and compact purple clay.

Drilling F6 is located on the right side of the National Road 64 that connects Rm. Valcea and Dragasani and on right side of Bistrita River at a distance of 1200 meters from drilling F5. Lithological description of this drilling indicates that layers sequence through which drilling F6 pass is: brown topsoil, yellowish sand with gravel, medium sand with gray purple gravel, boulders with compact sandy purple clay, purple micaceous sand, boulders and coarse sand with purple gravel, sandy purple clay.

Drilling F7 is located on the right side of the National Road 64 that connects Rm. Valcea and Dragasani and on left side of Bistrita River at a distance of 170 meters from drilling F6. Lithological description of this drilling indicates that layers sequence through which drilling F7 pass is: brown topsoil, sand with gravel, purple sand with rare items of gravel, medium and coarse sand with gravel items, coarse gravel with boulders, boulders and gravel big than 7 cm, boulders, medium purple sand, compact purple clay.

Drilling F8 is located on the right side of the National Road 64 that connects Rm. Valcea and Dragasani at a distance of 450 meters from drilling F7. Lithological description of this drilling indicates that layers sequence through which drilling F8 pass is: brown topsoil, brownie yellowish micaceous sand with rare items of gravel, gravel with boulders big than 7 cm in diameter and water, gravel and purple sand, coarse yellowish white sand, coarse sand with yellowish white gravel, purple and micaceous sand, low compact purple clay.

Water samples were collected from three wells located in the city Băbeni along flow path of studied aquifer. Wells are located on the right side of the National Road 64 at the following distances: well A to well B at 2260 m, well B to well C at 760 m and well C to drilling F8 at 400 m

Physico-chemical characterization

The importance of physico-chemical characteristics of the water sample has been shown not only for sampling of sufficient quantity of water, but also for analysis and interpretation of the radiocarbon results. Physico-chemical parameters determined for water sample are: pH, conductivity, bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), chloride (Cl^-), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), sulfates (SO_4^{2-}) and temperature.

Table 2. The physico-chemical characteristics of groundwater samples

No.	**Location**	**pH_i**	**C_i (μS/cm)**	**HCO_3^- (mg/l)**	**CO_3^{2-} (mg/l)**	**SO_4^{2-} (mg/l)**	**Cl^- (mg/l)**	**K^+ (mg/l)**	**Na^+ (mg/l)**	**Mg^{2+} (mg/l)**	**Ca^{2+} (mg/l)**
1	Drilling F1	7.84	381	220	-	24.3	9.60	1.42	25.61	9.11	34.95
2	Drilling F2	7.84	551	180	10	87.7	79.00	1.82	59.70	8.88	30.50
3	Drilling F3	7.14	2520	13	-	-	768.16	2.07	86.41	10.48	306.5
4	Drilling F4	8.93	1042	230	34	49.8	162.14	5.28	156.8	7.93	24.12
5	Drilling F5	8.81	463	250	11	110.0	23.00	1.70	41.00	8.00	31.00
6	Drilling F6	8.66	718	230	-	76.6	84.93	2.93	52.77	10.21	109.00
7	Drilling F7	8.82	565	190	-	90.6	61.80	2.43	51.50	6.85	34.70
8	Drilling F8	8.75	390	90	-	13.0	77.21	4.06	7.40	2.64	34.85
9	Well A	8.01	759	290	11	115	102.00	5.45	97.36	13.09	66.76
10	Well B	7.81	855	280	-	130	116.00	7.37	96.25	14.68	68.16
11	Well C	8.10	844	301	-	96.2	112.45	3.25	91.09	11.29	69.69
12	Olt River	8.93	837	110	-	33.3	6.90	3.02	57.00	5.63	70.50
13	Bistrița River	9.20	654	160	-	53.5	108.00	3.92	62.35	7.62	33.80

The above data were used as input in the PHREEQC software. Units used for anionic and cationic concentrations in water (mg / l) must be specified in the input data. From aqueous species equilibrium simulation is observed for all samples that bicarbonate is the dominant species and approaching as concentration value to the original data. The output data shows that all the solubility indices of hypothetical salts are negative, which means that saturation is not reached for any of the hypothetical carbon-containing salts found in water composition (aragonite $CaCO_3$, artinite $MgCO_3{:}Mg(OH)_2{:}3H_2O$, calcite $CaCO_3$, $CO_2(g)$, dolomite $CaMg(CO_3)_2$, dolomite(d) $CaMg(CO_3)_2$, huntite $CaMg_3(CO_3)_4$, hydromagnezite $Mg_5(CO_3)_4(OH)_2{:}4H_2O$, magnezite $MgCO_3$, nahcolite $NaHCO_3$, natron $Na_2CO_3{:}10H_2O$, nesquehonite $MgCO_3{:}3H_2O$, termonatrit Na2CO3:H2O, trona $NaHCO_3{:}Na_2CO_3{:}2H_2O$). In this conditions water samples stable in time and chemical precipitation of DIC to obtain barium carbonate being made in good condition even after a certain period of time.

Isotopic analyses

Determination of isotopic ratios $^2H/^1H$, $^{18}O/^{16}O$ and $^{13}C/^{12}C$ in collected water samples was made in "Laboratory of physico-chemical and environmental analyses and food quality (LAFMCA)" part of ICIT Rm. Valcea using a mass spectrometer with magnetic sector in continuous flow CF-IRMS Delta V Plus configured and designed for such analysis.

The minimum value of isotopic ratio $^{18}O/^{16}O$ has registered for Olt River and the maximum for Well A. Regarding $^2H/^1H$ isotope ratio minimum and maximum were recorded for Olt River, respectively Well A. From the below figure it can be concluded that all locations are influenced by precipitation, the average deuterium content being of local meteoric water. It can be seen that samples are grouped by isotopic content into three distinct groups: drills, wells and rivers. $\delta^{13}C$ values determined are used in applying of correction models that take into account this parameter.

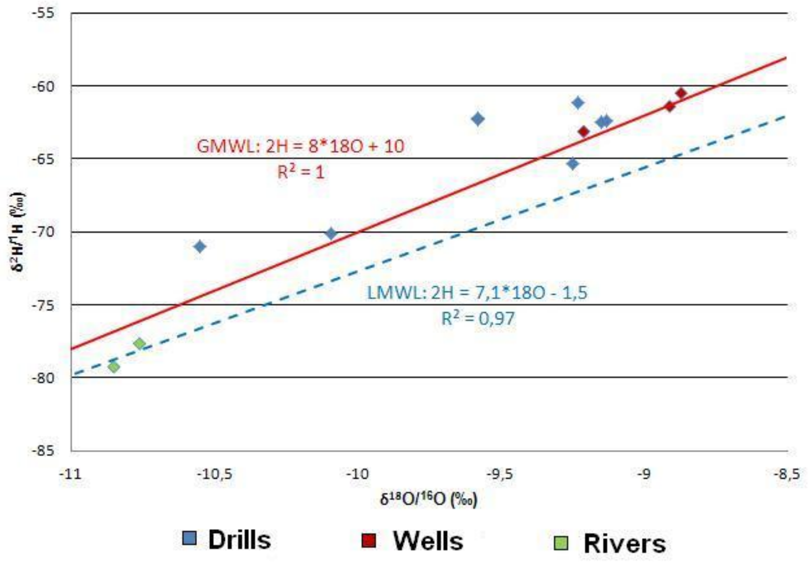

Figure 3. Variation of $^2H/^1H$ and $^{18}O/^{16}O$ isotopic ratio for analyzed samples

Determination of tritium activity concentration

Tritium concentrations of samples were performed using a liquid scintillation spectrometer, Quantulus 1220, built especially for environmental and low radioactivity samples. The figure below represents the variation of tritium concentration for analyzed samples and were identified following conclusions:

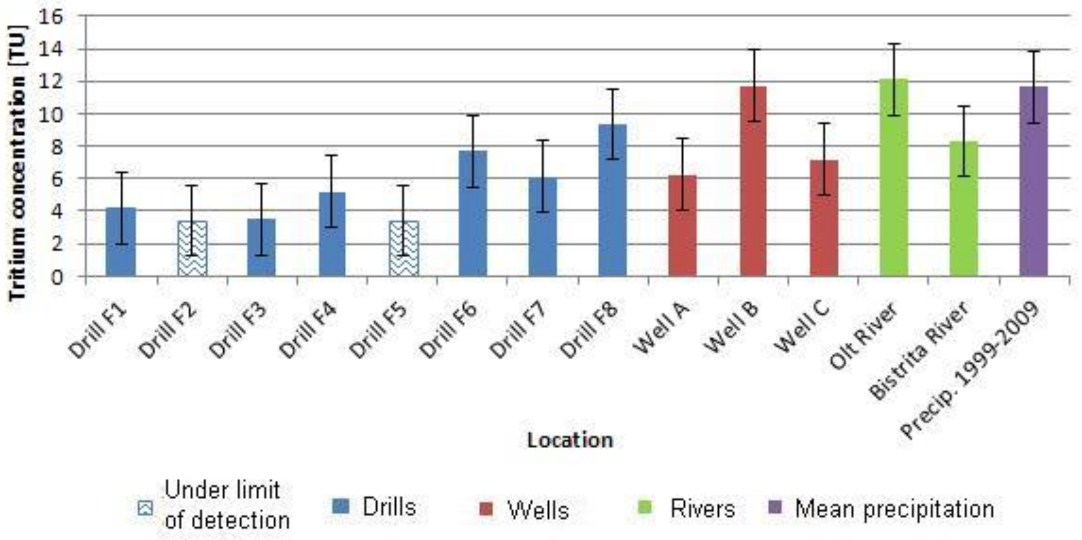

Figure 4. Variation of tritium activity concentration for analyzed samples

- tritium activity ranged between 12.10 ± 2.21 TU (Olt River) and activities below the detection limit (drillings F2 and F5). Maximum is found in surface water, which is expected, this being strongly influenced by precipitation. In studied area the tritium average activity weighted to annual rainfall is 11.62 ± 2.20 TU (observation period 1999-2009, Varlam, 2010);
- tritium concentration determined for Bistrita River was lower comparing Olt River and precipitation and this may indicate that the river has a groundwater contribution;
- tritium activity concentration determined for the three wells was found between 6.25 and 11.70 TU, the largest being determined Well B which indicates that it is probably mainly influenced by precipitation, in contrast to the other two for which groundwater contribution is likely to be significant;
- in terms of the tritium activity 8 drillings can be divided into two categories i.e. drillings with higher tritium concentrations (F6, F7 and F8) with activities ranging from 6.14 to 9.35 TU and drillings with low tritium concentrations (F1, F2, F3, F4 and F5) ranged between a maximum of 5.22 ± 2.10 TU and minimum below the

detection limit. If first category is clearly influenced by precipitation, for wells F1, F2, F3, F4 and F5 influence is less visible.

Underground water dating and age corrections using ^{14}C

Regarding the ^{14}C content, this was determined using procedures for the preparation and determination of ^{14}C activity concentration in water samples described in Chapter 5, section 5.4 of this paper. In brief procedures involve the following steps:

- preparation of scintillation cocktail by the method elaborated and optimized in the Tritium Laboratory of the National Research and Development Institute for Cryogenics and Isotopic Technologies - ICSI Rm. Valcea, from whose team I belong and where all the necessary experiments preparation of this thesis took place.
- precipitation of dissolved inorganic carbon (DIC) from the water sample in the form of barium carbonate;
- acidification of barium carbonate to obtain carbon dioxide;
- CO_2 absorption in scintillation cocktail;
- measurement of the specific activity of ^{14}C using liquid scintillation spectrometer Quantulus 1220.

The following are the values obtained for the 8 drillings and 3 domestic wells studied, the table summarizing all input data used to calculate age using correction models.

Table 3. ^{14}C specific activity used to determine and modeling of groundwater ages in studied locations

Location	**Counting rate (CPM)**	**Efficiency (%)**	**Activity (Bq)**	**^{14}C specific activity (Bq/gC)**	**$^{14}C_{DIC}$ (pMC)**
Drilling F1	6.778 ± 0.083	64.93	0.1068 ± 0.0025	0.14645 ± 0.0034	64,80
Drilling F2	6.269 ± 0.080	64.78	0.0937 ± 0.0024	0.13007 ± 0.00333	57,55
Drilling F3	3.984 ± 0.064	65.10	0.0352 ± 0.0021	0.23834 ± 0.01422	105,45
Drilling F4	7.845 ± 0.089	65.07	0.1341 ± 0.0024	0.19600 ± 0.00351	86,72
Drilling F5	6.485 ± 0.081	64.86	0.0992 ± 0.0025	0.14012 ± 0.00353	62,00
Drilling F6	8.135 ± 0.091	64.98	0.1415 ± 0.0027	0.21391 ± 0.00408	94,64
Drilling F7	8.412 ± 0.092	65.03	0.1486 ± 0.0027	0.22686 ± 0.00412	100,38
Drilling F8	6.329 ± 0.080	64.89	0.0952 ± 0.0024	0.24117 ± 0.00608	106,71
Well A	8.596 ± 0.0093	65.09	0.1533 ± 0.0027	0.22757 ± 0.00401	100,69

Well B	8.796 ± 0.0094	64.81	0.1584 ± 0.0028	0.22783 ± 0.00403	100,81
Well C	8.819 ± 0.0095	64.91	0.1590 ± 0.0028	0. 22511 ± 0.00396	99,60

Atmospheric radiocarbon concentration ($^{14}C_{atm}$) was considered to be 100 pMC, specific value before nuclear tests in the 60s. Regarding the isotopic ratio $\delta^{13}C$ I considered that its value is 0 ‰ for carbonate and -21 ‰ for soil CO_2, values that are used in the literature in such cases. Values of equilibrium constants K_1 and K_{CO2} for systems containing carbonate that we used to determine the chemical equilibrium reaction products were those for 25° C (Drever, 1997). For isotopic fractionation factors during carbon exchange system was used values for 25° C (Clark, 1999).

Using age correction models dilution factors for alkalinity correction (ALK model), chemical mass balance correction (CMB-Chem and CMB-Alk models), $\delta^{13}C$ model and matrix exchange (Fontes-Garnie model) were calculated. For statistical correction (STAT model) was chosen median value of the interval considered characteristic for substrate containing a fine-grained carbonate (0.75 - 0.90). Although calcite saturation is reached in the recharge area of most aquifers, especially for aquifers containing limestone rocks, like in case of studied aquifer in this paper, saturation is not reached, this being demonstrated by negative values of saturation index obtained for calcite from modeling with PHREEQC. For this reason the effect of magnesite dissolution was not considered and therefore this correction model was not applied. The figure below contains the dilution factor variation corresponding correction models considered.

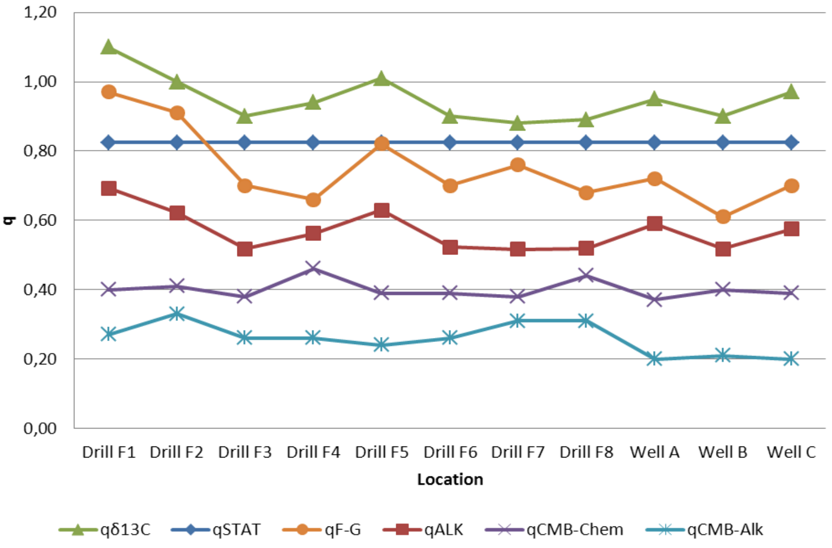

Figure 5. Variation of dilution factors corresponding correction models considered

Average values of the dilution factor is 0.949 for $\delta^{13}C$ model, followed by dilution factor for statistical correction model with a value of 0.825 and the dilution factor for Fontes-Garnie model with an average of 0.748. For alkalinity correction model and CMB-Chem and CMB-Alk models were determined average values of 0.569, 0.401 and 0.259 respectively. It should be noted that as the value of the dilution factor is closer to 1, the influence on age determination is lower.

Figure 6 contains the uncorrected and corrected ages with $\delta_{13}C$, STAT, F-G, ALK, CMB-Chem and CMB-Alk correction models.

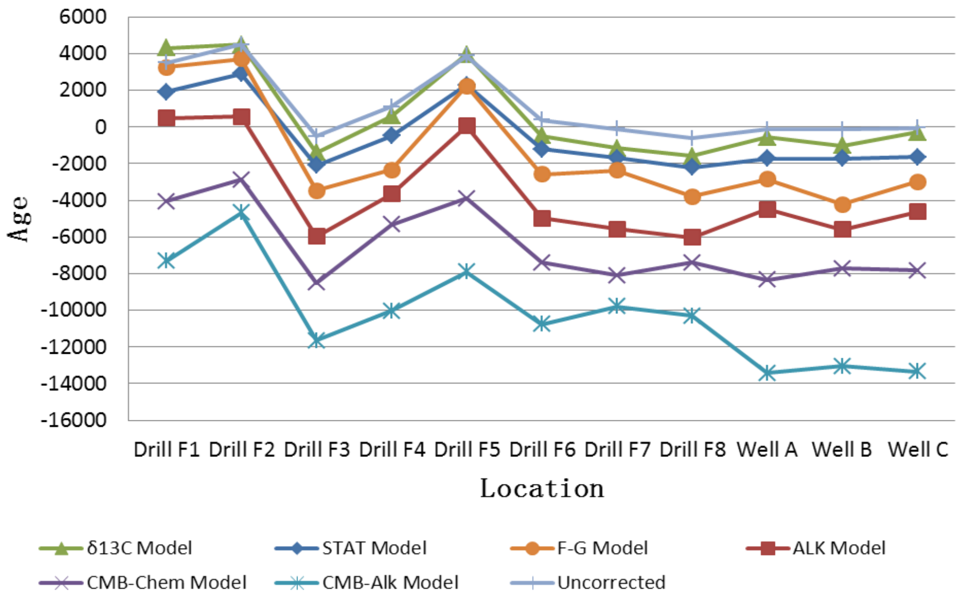

Figure 6. Variation of uncorrected and corrected age (years BP) using correction models considered

It is noted that the higher values were obtained for uncorrected ages because the uncorrected age assume that dissolution of carbonate take place only under open conditions, this being unlikely for studied groundwater body. These conditions are exceptional and related reactions due to exchange with the matrix and dolomite dissolution are not counted. On the other hand for models considering completely closed system (ALK, CMB-Chem and CMB-Alk models) corrections are much larger than necessary and therefore not really fit with the study. Consequently δ13C and F-G models, which assume that carbonate dissolution take place under a partially open system, are the most representative for the studied drillings and domestic wells. Table 4 contains age ranges found in the analyzed samples, according to values provided by the used models.

Table 4. Age ranges found in the analyzed samples and their average (in BP years)

Location	Age	Average
Drilling F1	~3200 – 4300	3782
Drilling F2	~3700 – 4500	4105
Drilling F3	Modern	-
Drilling F4	Modern	-
Drilling F5	~2200 – 3900	3100
Drilling F6	Modern	-
Drilling F7	Modern	-
Drilling F8	Modern	-
Well A	Modern	-
Well B	Modern	-
Well C	Modern	-

Interpretation of groundwater ages obtained by radiocarbon dating and subsequently corrected using correction models described in this thesis must always be done with as much information as possible. These include a good knowledge from hydrogeological point of view of studied aquifer and its recharged area. Dissolution of carbonates is often accompanied by other secondary processes such as sulphate reduction or dissolution of dolomite. For these reasons age itself should be used with caution, but nevertheless can provide useful information for estimating other aquifer parameters such as mean transit velocity of underground water. In practice, this parameter is considered more accurate and is obtained from the interpretation of relative values from radiocarbon dating for two collection points located on the flow pathway of groundwater. In table 5 are presented the average values of mean transit velocities of studied aquifer.

Table 5. Mean transit velocities of studied aquifer

Drillings	Mean age	Distance (m)	Velocity (m/year)
P1 – P2	322	500	0,6
P2– P5	1005	1980	0.5
		Mean	**0,55**

Mean transit velocity of studied aquifer is 0.55 m/year, value which is specific for this type of aquifer. This value was determined taking into account the difference in average age of drillings with old underground water and the distance between them. This parameter can be used both for sustainable development of studied area or to manage water resources much well taking account that water will be the most important natural resource due to climate change.

CONCLUSIONS AND PERSPECTIVES

Carbon (C) in an important chemical element of the biosphere, being the base of food chain and having a key role in every part of biogeochemical processes. Carbon dioxide (CO_2) is an important gas between greenhouse gases. Its concentration in atmosphere has grown from approximately 270 ppm, at the beginning of the industrial revolution, to approximately 360 ppm in the present. These changes in CO_2 concentration represent a global growth of approximately 30%, in less than 200 years. Processes which affect carbon cycle became of great interest in recent years, due to potential impact on the global climate.

Techniques for carbon cycle process studies that use its isotopes gaining ground due to increasing complexity advantages of analytical techniques and topics studied. Isotopic techniques provide tools for research regarding ways of exchange between atmosphere, biological systems and geological systems. Thus natural or anthropogenic changes of the concentration in carbon isotopes can be used to investigate carbon transfer between different systems in certain moments of time.

Carbon has three isotopes used as tracers, particularly useful in terrestrial ecosystems: ^{12}C stable isotope with an abundance of 98.89%, ^{13}C stable isotope with an abundance of 1.11%, and ^{14}C radioactive isotope with half-life of 5730 years. ^{12}C isotope is also called "light" carbon, compared with 13C and 14C isotopes, called "heavy" carbon isotopes. Natural production of ^{14}C, first postulated by Willard Frank Libby, takes place in the higher layers of the atmosphere, due to colliding of cosmic rays containing neutrons with atoms of nitrogen. Production rate was calculated from the total inventory of ^{14}C with a value of 1.0 x 1015 Bq / year, quite close to Libby's initial estimates of the flux of cosmic rays calculated (1.4 × 1015 Bq / year). ^{14}C is also produced in nuclear reactors and during testing nuclear weapons. Once produced, it is oxidized to $^{14}CO_2$ and in this form is incorporated into global carbon cycle through the same processes as $^{12}CO_2$ and $^{13}CO_2$. Consequently, any material that contains carbon derived from atmospheric CO_2 is potentially eligible for help radiocarbon dating.

Groundwater carbon cycle begins with chemical reactions from the recharge area. In the shallow groundwater geochemical evolution is dominated by bicarbonate reactions, those anions being dominant in freshwater bodies. Microbiological activity plays a key role in the decomposition of organic compounds and in the evolution of redox reactions. Understanding the evolution of carbonates and carbon cycle in groundwater is necessary to establish groundwater quality and the correct interpretation of groundwater age.

To simulate chemical reactions and transport processes in natural waters and contaminated water was used PHREEQC 2.10, a software developed by the U.S. Geological Survey. PHREEQC calculates, using reversible and irreversible geochemical reactions, elements concentration, molality and activities of aqueous species, pH, pe, saturation indices and interphase transfers necessary to reach equilibrium. The indicators used in this thesis that have been calculated with this software are saturation indices and aqueous species distribution.

In the world are aquifers with ages between decades and thousands of years. On the other hand groundwater that is part of the hydrological cycle is continuously renewed and its exploitation is sustainable. Deep groundwater may contain modern and old water, and anyway the presence of even a minor component of modern water is important because it indicates hydraulic connection of the aquifer with the groundwater. Consequently excessively exploitation may increase the contribution of modern component.

Modern groundwater is part of an active hydrological cycle and is considered refueled in the last few decades. Classical methods often give the best indication of whether groundwater is actively recharged. Some examples of such methods are: hydrogeological mapping, seasonal water level fluctuations, temporal variations of geochemical composition or composition of stable isotopes, identification of anthropogenic pollution (nitrates, etc.). However isotopes are used when hydrogeological characteristics are insufficient or inconclusive, and more importantly when determination of water age recently refueled is desired.

Geochemical evolution can be, and often is more complex, than the mathematical equations related to age correction models. The best way to correct the ages determined using radiocarbon is chosen depending on the particular geochemical groundwater system and on the available data. In general these models overestimate groundwater age, yet this age is closer to the true age than the uncorrected age.

NETPATH is interactive software, developed by the U.S. Geological Survey that uses concentrations of minerals and gases dissolved in water and isotopic composition of water from an underground reservoir at different points of testing, modeling and interpretation of groundwater ages obtained by radiocarbon being one of its options. The software uses the chemical and isotopic characteristics of samples from a groundwater body to examine all possible geochemical reactions and to determine the phases that may exist. Almost all models described previously in this paper are used in this interactive software, these being adapted and refined to work interdependently with input data used.

As original contribution can be emphasized the development, optimization and validation of the method, in order to obtain more precise results, the development of a clear procedure for investigating underground reservoir, which are not just about radiocarbon dating, but includes all needed parameters for groundwater management. Although radiocarbon measurement type proposed in this thesis is a classical one, optimizations to the preparation technique allow reduction of time and financial costs and can be successfully applied to a large number of samples, common in hydrological studies.

Experiments conducted on the development of water sample preparation procedure demonstrates that direct absorption technique developed and routine procedures developed in the laboratory lead to reproducible results with constant level of attenuation in samples prepared, results obtained validating the procedure of the laboratory for measuring ^{14}C by liquid scintillation.

To fulfill the objectives of this thesis we collected water samples from eight drillings, three domestic wells located further along the path of flow of aquifer and also two main rivers that influence the body of groundwater, river Olt and river Bistrița respectively.

Studied groundwater reservoir is located in the city of Băbeni, Vâlcea County, and drillings from which water samples were taken belong to Olt River Administration.

Physico-chemical indicators necessary to be determined, to be sure that we collected a sufficient amount of sample required for the analysis and also to make interpretation of the results from radiocarbon analysis and to use them in age determination, were: pH, conductivity and content of bicarbonate, carbonate, chloride, calcium, magnesium, sodium, potassium and sulphate. The obtained data were used as input data in the PHREEQC software. Output data showed negative solubility indices for all hypothetical salts calculated with PHREEQC software, which shows that saturation is not reached for any of the hypothetical carbon-containing salts found in water composition, thus the water samples keeping the composition in time and obtaining of barium carbonate precipitate being made in good condition, even after a certain period of time.

Regarding the isotopic ratios $^{18}O/^{16}O$ and $^{2}H/^{1}H$ it can be concluded that all locations are influenced more or less by precipitations, average deuterium content of water being that of local meteoric water. It can be seen that samples are grouped by isotopic content into three distinct groups: drillings, domestic wells and rivers.

From the analysis of the results that express the concentration of tritium in samples, we can identify the following conclusions:

- Measured tritium activity concentration ranged between 12.10 ± 2.21 UT (Olt) and activity concentrations below the detection limit (drillings F2 and F5). Maximum is found in surface water, which is expected, this being strongly influenced by precipitation, while the balanced annual average rainfall for tritium in this area is 11.62 ± 2.20 UT (observation period 1999-2009, Varlam, 2010)

- Regarding concentration of tritium found for Bistrita River, this was lower than average rainfall or Olt River and this may indicate that this river has a groundwater intake.

- Tritium activity concentration determined for the three domestic wells was found between 6.25 - 11.70 UT, the highest being Fountain B, which indicates that it is probably mainly influenced by precipitation, in contrast to the other two which seem to be considerably influenced by groundwater intake;

- Regarding concentration of tritium activity for the 8 drillings, those can be divided into two categories, namely drilling with higher tritium concentrations (F6, F7 and F8), with activities ranging from 6.14 to 9.35 UT, and drilling with lower concentrations tritium (F1, F2, F3, F4 and F5), with activities between 5.22 ± 2.10 UT and the detection limit. If the first category of drillings is clearly influenced by precipitation, the influence over drillings F1, F2, F3, F4 and F5 is less visible.

Regarding the uncorrected age can be observed that drillings F1, F2, F4, F5 and F6 have positive ages, which means that they are, on a first sight, old groundwater, while for drillings F3, F7, F8 and domestic wells A, B and C were obtained negative ages, which, corroborating with tritium activity concentration and $^2H/^1H$ and $^{18}O/^{16}O$ isotopic ratios, can conduct to the conclusion that water samples taken from these locations are modern water coming from precipitation.

Dilution factors were calculated for alkalinity correction (ALK model), chemical mass balance correction (CMB-Chem model and CMB-Alk), $\delta^{13}C$ and exchange matrix model (Fontes-Garnie model). Dilution factor for $\delta^{13}C$ model is the largest, with an average of 0.949, followed by dilution factor for statistical correction model, with a value of 0.825 and the dilution factor from Fontes-Garnie model, with an average of 0.748. The smallest dilution factors were obtained for alkalinity correction model and Chem CMB and CMB-Alk models, with average values of 0.569, 0.401 and 0.259 respectively.

By applying the δ13C model for drillings F1, F2, F4 and F5 positive ages were obtained, while for the other drillings and domestic wells negative ages were obtained. By running statistical model negative ages were obtained for all locations except drillings F1, F2 and F5. By applying Fontes-Garnie model positive ages resulted for drillings F1, F2 and F5 and negative for other drillings and wells. The ages resulting from applying ALK correction model were negative for most samples analyzed. Age correction using CMB-Chem and CMB-Alk models conducted to negative ages for all samples analyzed.

Models that consider completely closed system (ALK model, CMB-Alk and CMB-Chem) make corrections much larger than necessary and therefore are not really fit with the study, and therefore $\delta^{13}C$ and Fontes-Garnie models, that assume the carbonate dissolution under a partially open system, are the most representative for studied drillings and wells. According to figures provided by these models, ranges in which ages can be found are: for drilling F1 ~ 3200-4300, for drilling F2 ~ 3700-4500 and for drilling F5 ~ 2200-3900.

Ages themselves should be used with caution, but nevertheless can provide useful information for estimating water reservoir parameters, such as mean transit velocity of groundwater. In practice this parameter is considered more accurate and is obtained from the interpretation of relative values from radiocarbon dating for two collection points located on the line of groundwater flow. This parameter can be used both for sustainable development on medium and long term of the studied area and for water resource management, giving the fact that due to climate change water will be the most important natural resource. For aquifer studied transit velocity was calculated to 0.55 m/year.

In conclusion, use of groundwater ^{14}C dating is irrelevant without some basic steps identified through this work, namely:

- Lithological characterization of the sampling points;
- In-situ characterization of water sample (minimum pH, temperature, conductivity and alkalinity, parameters that may change during transport and storage);
- Chemical characterization of the water sample (main anions and cations);
- Determination of isotopic ratios for stable isotopes of hydrogen, oxygen and carbon;
- Establishing saturation indices and identification of major carbon species (HCO_3^-, CO_3^{2-}, etc.);
- Measurement of the radiocarbon specific activity and its normalization to determine the age;
- Selection of appropriate models for age correction, corroborating lithological, physico-chemical and isotopic information;
- Determination of the average transit speeds and the protection of the underground reservoir.

This procedure is successfully applied in our institute, equipped with the necessary infrastructure necessary to accomplish all investigations above described, to determine the age and degree of protection of a groundwater reservoir.

In perspective the correlation of these investigations with nitrogen isotopes can be done, to identify its sources in groundwater reservoirs, given the fact that the legal maximum limits for nitrates, nitrites and ammonium in drinking water are very low, 50 mg / l NO_3^-, 0.5 mg / l NO_2^- and 0.5 mg / l NH_4^+. The same regulations stipulate that concentration of organic and inorganic nitrogen should not exceed 1 mg/ l, but if it is demonstrated that the presence of NH_4^+ is of endogenous origin, that limit is 5 mg / l.

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