USE OF C-14 AND ENVIRONMENTAL ISOTOPES TO ESTIMATE AQUIFER RECHARGE CONDITIONS

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This paper combines radiocarbon age and other environmental isotopes to estimate recharge conditions to a local groundwater aquifer. Estimation was carried out using $^{14}$C and other environmental isotopes, such as tritium, deuterium and oxygen-18. Three types of samples were used: rainfall, surface water and underground water. Radiocarbon and tritium measurements were carried out using liquid scintillation counting. Deuterium and oxygen-18 isotopic composition was determined by mass spectrometry. Mean transit velocities in upper part of aquifer located in volcanic-sedimentary formations was in a range between 0.2 and 1.3 m/year with mean value of 0.9 m/year. Mean transit velocity, specific to aquifers ensemble located in stratovolcanic andesite formations and volcanic-sedimentary formations, is about 2.3 m/year. Results obtained together with similar data from nearby areas, are sufficient to estimate recharge conditions of studied aquifer.

Key words: Radiocarbon, environmental isotopes, groundwater, aquifer.

1. INTRODUCTION

The use of $^{14}$C data in ground water age has a large application in hydrology because of lack of alternative dating tools for ages from few thousands years to $4 \times 10^5$ years. $^{14}$C data can be used to constrain water flow direction and velocities, fluxes, recharge rates, hydraulic conductivities, and effective porosity. In hydrology, rock layer that contains water can release it in appreciable amounts. The rock contains water-filled pore spaces, and, when the spaces are connected, the water is able to flow through the matrix of the rock. An aquifer also may be called a water-bearing stratum, lens, or zone. A confined aquifer is a water-bearing stratum that is


confined or overlain by a rock layer that does not transmit water in any appreciable amount or that is impermeable. There probably are few truly confined aquifers, because tests have shown that the confining layers, although they do not readily transmit water, over a period of time they contribute with large quantities of water by slow leakage to supplement production from the principal aquifer. A groundwater aquifer is classified to be unconfined when its upper surface (water table) is open to the atmosphere through permeable material.

$^{14}$C dating of ground water is a challenging task and in many cases of this kind of data must be used with precaution or correlated with environmental isotopes (tritium, deuterium, $^{18}$O, $^{13}$C) at least. Important corrections to apparent $^{14}$C ages are often imposed because dissolved inorganic carbon (DIC) in ground water sample is a mixture of carbon from different sources. In this paper are presented preliminary results for the estimation of aquifer recharge condition using $^{14}$C data and environmental isotopes of studied areas. The traditional formula approach for correction of apparent ages are used, but more holistic inverse mass balance modeling approach (Chen Zhu and Murphy W.M., 2000) will be used after a much longer period of hydrological observations.

2. METHODS, EQUIPMENT AND MATERIALS

Studied aquifer is located in volcanic-sedimentary formation of Neogene age. This impermeable formation is crossed and covered mostly by andesites, but may have accumulation and transit areas through which water can infiltrate from the surface. Estimation of aquifer recharge conditions was carried out using C-14 and other environmental isotopes, such as tritium, deuterium and Oxygen-18. Different types of samples were collected: rainfall, surface water, well water, and underground water. The drilling locations were established for shallow depth, approximately 30 m, and deep depth, between 50 and 120 m.

The method used for determining $^{14}$C concentration in the water samples was the direct absorption method followed by liquid scintillation counting (LSC) with an ultra-low level liquid scintillation spectrometer Quantulus$^\text{TM}$ 1220. The beta activity of the samples corresponding to its $^{14}$C decay is measured and is compared to that of the background and modern $^{14}$C standard (Varlam et al. 2007). The method applied in our laboratory for $^{14}$C analysis of water samples (using the method of direct absorption of CO$_2$ in a mixture scintillation solution) has 4 steps. The first step after receiving the samples is the preparation of the LS cocktail, which contains a tertiary amine, fluorescence substances, and solvents. In the second and the third steps, dissolved inorganic carbon (DIC) is precipitated and then acidified to release CO$_2$. In the fourth and final step, the CO$_2$ is transferred to a bladder in the bubbling line and then bubbled through the liquid scintillation solution for
10 minutes to ensure saturation of amine with the CO₂ as carbamate (Varlam et al., 2006). The vials are then counted via conventional ^14C analysis. Applying the validation procedure it was established a mean activity for marine shell of 0.2178 ± 0.0039 Bq/g C that translate to 114.18 ± 1.82 pMC, referred to the decay corrected 95% NBS oxalic acid activity and adjusted to δ^{13}C = −25‰. Each ^14C activity was corrected by its individual δ^{13}C. Determination of CO₂ and HCO₃⁻ molar fractions was needed in order to be able to apply correction models of the initial activity of ^14C. Applied models were Pearson Model and Fontes-Garnier Model. Using chemical characterization of water samples was made a lot of simulations using Phreeqc. 2.10 and database “wateq4f.dat” to establish CO₂ and HCO₃⁻ molar fractions.

Tritium, the radioactive isotope of hydrogen with atomic weight of approximately 3, has a half-life of 12.32 years; it occurs in natural water with an abundance of 10⁻¹⁸ of that of natural hydrogen. Due to its low activity in the environment tritium unit (TU) is the unit used in environmental tritium activity and hydrological studies (1 TU means one tritium atom to 10¹⁸ hydrogen atoms). One TU corresponds to 0.11919 ± 0.00021 Bq/kg. The following numerical constants and parameters were used to convert TU to Bq/kg: Avogadro constant NA = 6.022114199 (± 0.000000047) × 10²³/mol; molar mass of water m_{H₂O} = 0.01801528 kg/mol; tritium half life T_{1/2} = 4500 ± 8 days; tritium decay constant λ = 1.5403 (± 0.0027) × 10⁻⁴ days. The specific activity of natural water samples is so low that to obtain accurate measurements any counting system must have a high and stable overall efficiency for the detection of low energy β particles together with a low and stable background. Method used for determination of the tritium content consists in the measurement in an ultra low-level liquid scintillation spectrometer of the water samples. Previously, by chemical treatment with sodium thiosulphate and carbonate, and then by distillation of the dissolved salts, the interfering organic matter and the radioactive volatile substances have been removed. The specific conditions used in our laboratory were: 20 ml polyethylene vial, UltimaGold uLLT scintillation cocktail, 8:12 ml ratio water: scintillate, 1000 minutes counting time, and a low limit of detection according to SR ISO 9698/1998 around 4.4 TU with 0.674 CPM background and efficiency of 25.78%.

The δ¹⁸O contents were measured by equilibration of 3 ml water with CO₂ and measurement of the isotopic ratio of CO₂ using an ATLAS 86 mass spectrometer equipped with a double collector and double inlet system. The deuterium analyses of water were carried out with a home-made mass spectrometer SMAD-1 on the hydrogen gas obtained by on-line quantitative reduction of about 1 ml water sample. The isotopic contents were expressed as δI value in “parts per thousand”:

\[ \delta I = \left( R / R_s - 1 \right) \cdot 1000, \]

where: I = D or ^18O isotopes, R = the isotopic ratio of sample, R_s = the ratio of international V-SMOW (Vienna Standard Mean Ocean Water) standard; the precision of δ ^18O measurements is ± 0.2‰; the precision of δ D values is ± 2‰ (Berdea et al., 2005).
3. RESULTS AND DISCUSSIONS

Five samples P5, P6, P7, P8 and P9 along flow line of aquifer were analyzed for $^{14}$C measurements. Results are expressed in percent modern carbon (pMC), representing the proportion of $^{14}$C activity in the sample compared to the $^{14}$C standard activity. Standard activity is defined as 95% of the activity of oxalic acid I in AD 1950 (Mook et al. 1999), and 100 pMC = 226 Bq/kg C. In Table 1 are presented values obtained for the analyzed samples and apparent age. Initial activity of $^{14}$C and age of the sample obtained by applying Pearson Model and Fontes-Garnier Model are also presented in the table.

<table>
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<td>2429</td>
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Mean of all analyzed samples 3895

The mean transit velocities in the upper part of the aquifer located in volcanic-sedimentary formations was in a range between 0.2 and 1.3 m/year with a mean of 0.9 m/year. These values were obtained taking care of differences between $^{14}$C mean ages of samples from drillings P5, P8 and P9 and distances between them. Samples P6 and P7 were not considered due to small distance between these drillings reported to specific errors of radiocarbon dating method. Mean transit velocity is about 2.3 m/year, which is a specific value to aquifers ensemble located in stratovolcanic andesite formations and volcanic-sedimentary formations. In Table 2 are presented obtained results.

<table>
<thead>
<tr>
<th>Drillings</th>
<th>Mean age [years BP]</th>
<th>Distance [m]</th>
<th>Transit velocity [m/year]</th>
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<td>P5 – P6</td>
<td>2140</td>
<td>500</td>
<td>0.2</td>
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<td>P5 – P8</td>
<td>961</td>
<td>1240</td>
<td>1.3</td>
</tr>
<tr>
<td>P5 – P9</td>
<td>2417</td>
<td>2680</td>
<td>1.1</td>
</tr>
<tr>
<td>P8 – P9</td>
<td>1456</td>
<td>1460</td>
<td>1.0</td>
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</table>

Mean transit velocity 0.9

For tritium measurements were analyzed annual precipitation, four surface water and well samples, eight samples from drillings along flow line of aquifer and two samples from deep drillings. The mean tritium concentration in annual
precipitation was $12.9 \pm 2.1$ TU, and in surface water $12.4 \pm 2.1$ TU. Tritium concentration measured in wells (K1 and K3) and surface water (V1 and V3) was between 6.9 and $9 \pm 2.1$ TU. The aquifer situated in upper part of volcanic sedimentary formation (P2 to P11) had a tritium concentration between $0.7 \pm 2.1$ TU and $4.9 \pm 2.1$ TU (Fig. 1).

Deuterium and oxygen-18 isotopic composition was determined by mass spectrometry in rainfall, surface water and underground water in the same location as for tritium measurements. The results of the deuterium and oxygen-18 measurements are given on Fig. 2.

![Fig. 1. Tritium concentration of samples from studied area.](image1)

![Fig. 2. Deuterium and oxygen-18 isotopic composition of samples from studied area.](image2)
This diagram shows the meteoric origin of samples having the average deuterium content of local meteoric water. Following equation describe Local Meteoric Water Line:

\[
\delta D(\text{‰}) = 6.1 \cdot \delta^{18}O(\text{‰}) + 13.6
\]

Deuterium and oxygen-18 isotopic composition values show four distinct groups similar to tritium content: shallow drillings, wells, surface water, and rainfall.

4. CONCLUSIONS

Estimation of aquifer recharge conditions was carried out using C-14 and other environmental isotopes, such as tritium, deuterium and oxygen-18. Different types of samples were collected: rainfall, surface water, well water, and underground water. The drilling locations were established for shallow depth, approximately 30 m, and deep depth, between 50 and 120 m.

The mean tritium concentration in annual precipitation was 12.9 ± 2.1 TU, and in surface water 12.4 ± 2.1 TU. Tritium concentration measured in well was between 6.9 and 9 ± 2.1 TU. The aquifer situated in upper part of volcanic sedimentary formation had a tritium concentration between 0.7 ± 2.1 TU and 4.9 ± 2.1 TU.

The mean transit velocities in the upper part of the aquifer located in volcanic-sedimentary formations was in a range between 0.2 and 1.3 m/year with mean value of 0.9 m/year, taking care of distances between drillings and C-14 measurements. Mean transit velocity is about 2.3 m/year, which is a specific value to aquifers ensemble located in stratovolcanic andesite formations and volcanic-sedimentary formations.

Although volcanic-sedimentary formations are considered more conductive than andesites, in our particular case it was emphasized the reverse situation, at least in the upper part investigated by shallow drillings.

Number and frequency of measurements carried out do not allow the formulation of accurate quantitative conclusions, but our study will be continued over a minimum period of one hydrological year.

REFERENCES